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# DIELECTRIC CONSTANT, POWER FACTOR, AND RESISTIVITY OF RUBBER AND GUTTA-PERCHA

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## ABSTRACT

A careful study has been made of the dielectric constant, power factor, and resistivity of rubber and its compounds, and of gutta-percha. Crude rubber has a lower dielectric constant than either gutta-percha or vulcanized rubber, the value of the latter depending on the conditions of vulcanization. Vulcanization by sulphur alone produces a higher dielectric constant than vulcanization with the aid of an accelerator. The addition of a filler generally increases the dielectric constant, sometimes by as much as 200 or even 300 per cent. Dried samples of both rubber and gutta-percha have a lower dielectric constant than those which contain absorbed water. Vulcanized rubber may have a lower dielectric constant than gutta-percha.

The power factor of crude rubber is about the same as that of gutta, the hydrocarbon of gutta-percha. Vulcanization of rubber increases the power factor, but the increase is less if vulcanization is effected by the use of an accelerator than when sulphur alone is used. The addition of quartz as a filler decreases the power factor, but most fillers increase this constant. The power factor of gutta-percha is higher than that of gutta, the amount depending on the per cent of resin.

Crude rubber, vulcanized rubber, and gutta-percha all have about the same resistivity. The incorporation of some substances in vulcanized rubber increases the resistivity. This is true of litharge in certain proportions. However, other substances produce a decrease in resistivity, this being especially true of carbon. Small amounts of absorbed water lower the resistivity.

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## I. INTRODUCTION

This investigation <sup>1</sup> was undertaken to determine the suitability of rubber as an insulating material for submarine cables. It has consisted in measuring the dielectric constant, power factor, and resistivity of specially prepared samples. These samples were made for the purpose of showing the effect of methods of preparation and subsequent treatment on the above electrical properties. While these particular properties were chosen on account of their importance in submarine-cable operation, the results are of value in other insulation fields.

For any particular purpose, other physical properties may be quite as important as the electrical properties. These have to some extent been studied, but the data are not as yet sufficient to permit the

<sup>1</sup> The Signal Corps of the U. S. Army requested the investigation, supplied the funds for the first two years' work, and has contributed to the expense since then.



drawing of definite conclusions. For submarine cables the most important property, aside from the electrical properties, is the deterioration with age. Considerable time is necessarily required to get useful data.

The most important electrical constant of the insulating material of a submarine cable is the dielectric constant. This should be as low as possible. It was shown by Kelvin that, as a first approximation, the relative speed with which signals can be transmitted over two cables is inversely proportional to the ratio of the dielectric constants, the cables being identical in other respects. Hence, other things being equal, materials which have low dielectric constants are most suitable for submarine cables.

For locating faults in submarine cables it is important that the resistance between the conductor and the surrounding water should be relatively high, say one hundred times the resistance of the conductor. This requires, for a transoceanic cable, that the resistivity of the insulating material shall be high, say about  $10^{15}$  ohm-centimeters. However, no unusual difficulty is experienced in obtaining materials having this resistivity. It is therefore only necessary to determine that the resistivity will not fall below  $10^{15}$  ohm-centimeters under working conditions.

The electric absorption of a cable causes any given signal to be affected by those which have preceded it. Hence it is desirable that the absorption shall be small. There is no simple way of measuring the absorption. However, those materials which have low absorption have low power factor. For submarine-cable design the absorption can be sufficiently well estimated from values of the power factor. As the power factor can be easily measured, this property has been determined rather than attempting measurements on absorption.

No systematic measurements have been made on the dielectric strength. It is not an important constant of submarine-cable insulation, since the applied voltage is always low. Moreover, there is so much uncertainty in the interpretation of dielectric strength results that it has seemed best to leave this for a special research.

In attacking this problem an attempt has been made to measure first the constants of crude rubber and of gutta-percha and then to determine the effect of compounding with other materials. The materials which were chosen for study are mainly those which are of commercial importance. In some cases compounding materials have been used on account of their theoretical interest.

The most important compounds of crude rubber are those with sulphur. When rubber and sulphur are mixed together and heated they combine in any ratio from 100 per cent rubber-0 per cent sulphur, to 68 per cent rubber-32 per cent sulphur. The reaction

which rubber undergoes with sulphur, along with the accompanying change in physical properties is called vulcanization or curing of the rubber, and the resulting compound, vulcanized rubber. Small amounts of sulphur change crude rubber to the soft rubber of everyday use, while larger amounts give rise to ebonite or hard rubber. The properties of the product depend not only on the amount of sulphur which was mixed with the rubber, but also on the time and temperature of vulcanization.

The nature of the reaction between rubber and sulphur is not clearly understood. When the proportion of sulphur used is large the chemical compound  $(C_5H_8S)_x$  is formed. With smaller proportions of sulphur to rubber no definite compounds have been isolated. Either a large number of chemical compounds of rubber and sulphur are possible or the few compounds that can be formed are miscible with each other and with rubber in all proportions.

A rubber-sulphur mixture vulcanizes more readily if there has been added to it a small quantity of any one of a certain group of compounds called accelerators. These accelerators are not merely catalysts since they may also markedly modify the nature and properties of the resulting vulcanized rubber. By their use the time and temperature of vulcanization have less influence on the resulting product. Hence by employing accelerators a greater uniformity in vulcanized rubber can be obtained.

For many purposes the properties of rubber can be improved by adding some inert material called a filler. Fillers may be used in any proportion from 0 to 90 per cent. The rubber, filler, and sulphur are mixed together before vulcanization. The vulcanizing process does not change the chemical nature of the filler. However, the mechanical and electrical properties of the rubber may be greatly modified by its presence.

The mixtures of rubber, filler, and sulphur are somewhat difficult to work, so that softeners are often added to facilitate the working of the mixtures. These softeners are bituminous, asphaltic, or waxy materials. They are used in relatively small amounts and apparently do not combine with any of the other materials in the mixture.

This investigation was undertaken to determine the relative suitability of rubber, rubber compounds, and gutta-percha for submarine-cable insulation. It has consisted in the measurement of the dielectric constant, power factor, and resistivity on specimens which have been especially prepared for this work. The results should be useful not only in connection with submarine cables, but wherever rubber is used as an insulating material.

## II. METHODS OF MEASUREMENT

In order to obtain the electrical constants of a material it is necessary that it be in a form suitable both for electrical measurements and for a measurement of its dimensions. As shown later, flat sheets have been used in this investigation in all determinations of the electrical constants when a knowledge of the dimensions is required. With specimens of this form, the errors in the resulting dielectric constant may be due either to errors in the measurement of the dimensions or to errors in the electrical measurements, since both kinds of measurement can be made with about the same accuracy. Errors in power factor and resistivity are practically all due to errors in the electrical measurements.

There is no object in making the electrical or dimensional measurements with greater accuracy than is warranted by the reproducibility of the specimens. For example, if two specimens supposedly identical give results which differ by 10 per cent, there is nothing to be gained by making the electrical measurements with an accuracy greater than 1 per cent.

When this work was started the dielectric constant of two supposedly identical specimens would frequently differ by 10 or even 20 per cent, the power factor of one might be double that of the other, while the resistivity of one might be ten times that of the other. With such samples there was no object in making precise electrical measurements.

As the work progressed methods of improving the quality of the samples were devised. At the present time the dielectric constant of two identical samples seldom differs by more than 3 per cent, the power factor by more than 30 per cent, and the resistivity by more than 100 per cent. This improvement in the reproducibility of samples has required a corresponding improvement in the accuracy of measurement. The following description will cover not only the final methods, but also some of those which were used in the earlier part of the investigation.

### 1. DIELECTRIC CONSTANT

The dielectric constant has been determined by measuring the capacitance of a condenser, the dimensions of the dielectric of which could be measured. While some comparative measurements have been made on tubes and insulated wires, most of the actual determinations of the dielectric constant have been made on sheets. This requires three measurements—the capacitance of a condenser, the thickness of the dielectric, and its area. All are needed with the same percentage of accuracy.



## (a) MEASUREMENT OF THE AREA

The area can readily be measured. In all cases the specimens are circular, or nearly circular. Several diameters are measured by a steel scale and the area computed from the average diameter. The value can very readily be determined with an accuracy of 1 per cent.

## (b) MEASUREMENT OF THE THICKNESS

The accurate measurement of the thickness of the specimen is difficult. The total thickness is not over 1 or 2 mm, and even good sheets will vary from point to point by as much as 0.1 mm. To obtain the average thickness with an accuracy of 1 per cent requires that the measurements be made at a number of points which are distributed over the surface according to some systematic pattern.

A pattern which has been found satisfactory is shown in Figure 1. It requires measurements at 19 different points, distributed uniformly over the specimen. Check measurements indicate that when the maximum variation in thickness is less than  $\pm 10$  per cent, measurements by the above pattern will give the average thickness with an accuracy of 1 per cent.

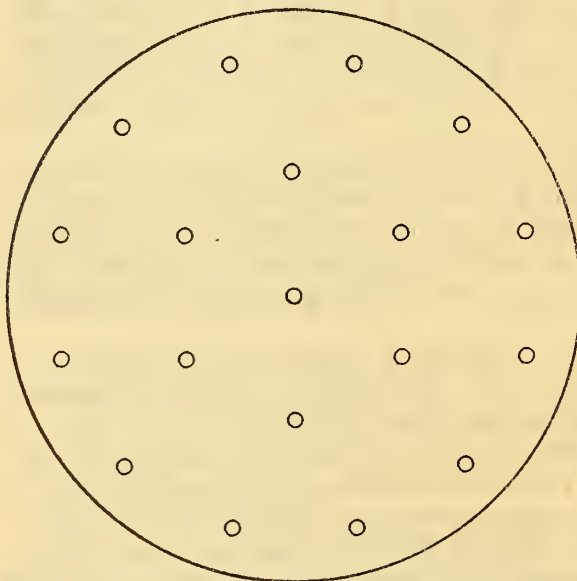


FIG. 1.—Pattern to indicate the spacing of points for thickness measurements of sheet specimens

In computing the dielectric constant of a material whose thickness is not uniform it can be shown that a more accurate result is obtained by taking the average of the reciprocals of the thicknesses rather than the reciprocal of the average thickness. If the thickness is measured directly, considerable labor is involved in reading the reciprocals from a table, recording, and averaging them. In order to reduce this labor a special dial was constructed for a dial gauge on which the reciprocal of the thickness is read directly. This gauge is shown in Figure 2. While the range of this scale is very limited, viz,  $\frac{1}{4}$  to  $1\frac{1}{4}$  mm, it is sufficient for the specimens used in this investigation.

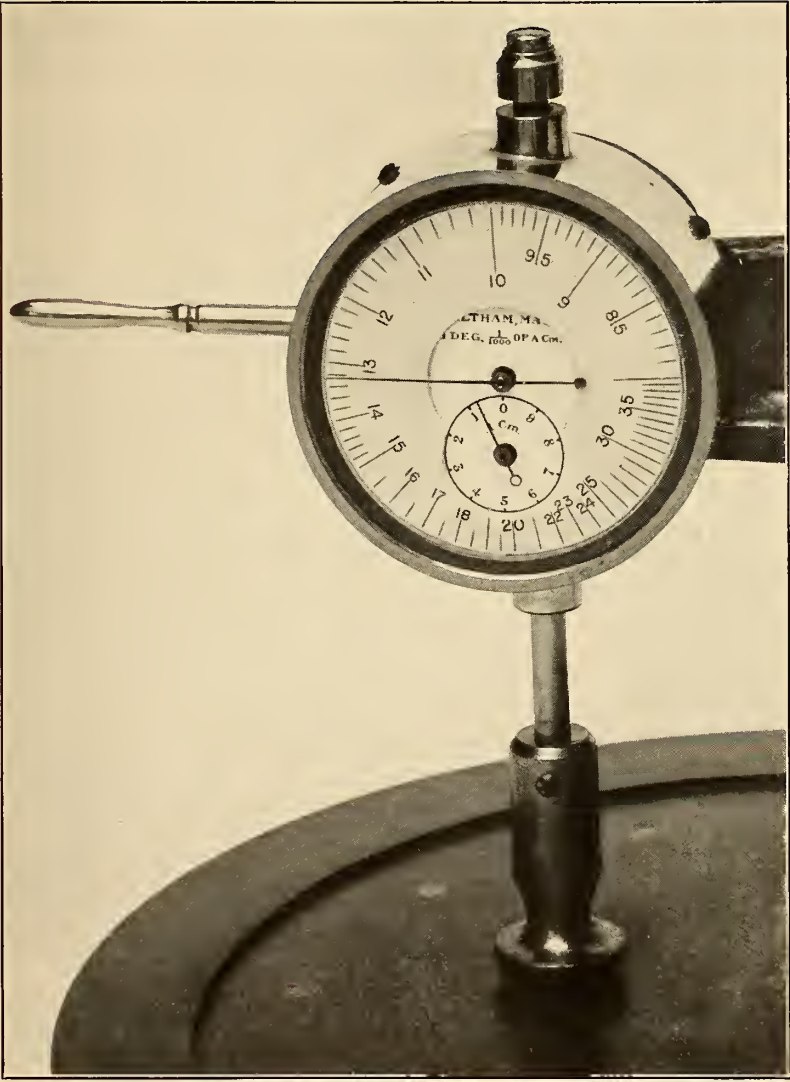


FIG. 2.—Thickness gauge showing reciprocal dial





## (c) MEASUREMENT OF THE CAPACITANCE

The capacitance has been measured by both direct-current and alternating-current methods. These methods have previously been described, but they have been somewhat altered to meet the needs of this research. Hence they will be given in some detail.

a. ALTERNATING-CURRENT METHODS.—For the alternating-current measurements, the Rosa bridge,<sup>2</sup> as shown in Figure 3, has been used. The current is supplied by a transformer which has two identical coils that can be connected in series. The point where the two coils are joined is grounded. By this arrangement the bridge terminal *A* is always as much above (or below) earth potential as *B* is below (or above). Hence if the two condensers have the same value the detecting instrument will remain at earth potential and the balance will not be affected by any earth capacitances in this arm.

The resistance of the arms *AG* and *GB* are made equal. The value of this resistance has usually been 1,000 ohms, but any value between 100 and 1,000 ohms is satisfactory. A variable inductor *L* of suitable range is included in *AG* and a fixed inductor *N* having an inductance approximately equal to the maximum value of *L* is included in *GB*. The maximum value of the capacitance of both the auxiliary air condenser *C*<sub>1</sub> and the standard air condenser must be as large as the capacitance of the specimen to be considered. A vibration galvanometer is used as a detecting instrument if the

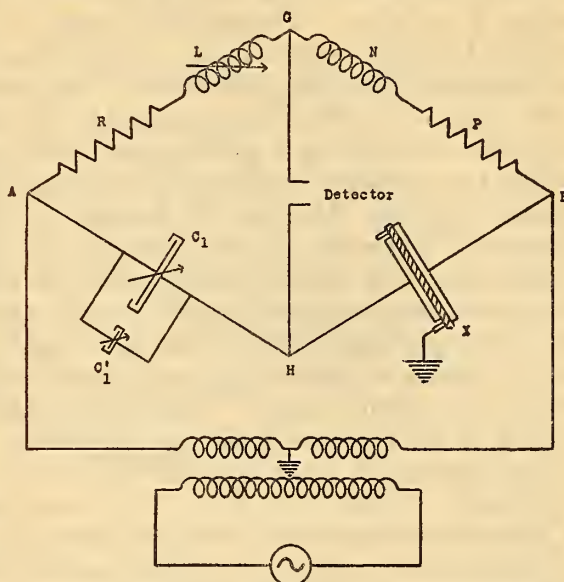


FIG. 3.—Diagram of Rosa bridge showing the specimen, *X*, connected in one arm

To make a measurement of the capacitance and power factor of a specimen, first adjust *C*<sub>1</sub> and *L* for a balance. Replace the specimen by the standard air condenser, connecting the earth terminal to *H*. Balance by adjusting *L* and the standard air condenser. The capacitance of the standard air condenser is that of the specimen. The power factor is

$$F = \frac{p(L_s - L_x)}{R}$$

where *p* is  $2\pi$  times the frequency; *L*<sub>s</sub> and *L*<sub>x</sub> are the readings of the variable inductor when the standard air condenser and the specimen, respectively, are in the bridge.

<sup>2</sup> Grover, The Simultaneous Measurement of the Capacity and Power Factor of Condensers. B. S. Bul., 3, 389; 1907 (B. S. Sci. Paper No. 64).

frequency is 100 cycles or less; for higher frequencies a telephone is used.

In making a measurement the specimen is inserted in *HB* and the bridge balanced by varying  $C_1$  and  $L$ . To facilitate this, a small-valued variable condenser  $C'_1$  is placed in parallel with  $C_1$ . It is not necessary to know the values of  $C_1$  or  $C'_1$ . When a balance has been obtained the specimen is removed and the standard condenser inserted in its place. The bridge is again balanced by varying the standard air condenser and  $L$ . Then the reading of the standard air condenser<sup>3</sup> gives the capacitance of the specimen.

**β. DIRECT-CURRENT METHODS.**—The direct-current capacitance has been measured by a modification<sup>4</sup> of the method of mixtures in which the operation of charging, discharging, and mixing are repeated at regular intervals. A diagram of the method is shown in Figure 4. The speed of the driving motor is adjusted so that the commutator arm makes a revolution in two seconds. The length of the commutator segments is such that the condensers are charged for 0.5 second insulated for 0.1 second, and allowed to mix for 0.1 second or 1.0 second, depending on the galvanometer connection. At the end of the mixing period, the galvanometer is momentarily connected to the junction of the two condensers. By adjusting  $R_1$  or  $R_2$ , a condition is reached when there is no deflection of the galvanometer. Then  $C_1R_1 = C_2R_2$ . If  $C_1$  is an air condenser, and  $C_2$  a specimen which shows absorption phenomena, then as the time of mixing is increased, more of the absorbed charge is released from the specimen, so that the apparent capacitance increases. Hence the increase of the capacitance when the time of mixing (or length of discharge) is increased gives a measure of the absorption of the specimen. This type of measurement is difficult to make on small specimens. The measurements have been confined to a few specimens in the form of wires and tubes.

<sup>3</sup> The capacitance  $K$  of the specimen is not strictly equal to the capacitance  $C$  of the standard air condenser but is given by the equation

$$K = C \frac{R^2 + p^2 L_x^2}{R^2 + p^2 L_x L_a}$$

where  $p$  is  $2\pi$  times the frequency,  $L_x$  the inductance of the variable inductor when the specimen is in the bridge, and  $L_a$  is the inductance when the standard air condenser is in the bridge. The correction term is zero if  $L_x = 0$  or if  $L_x = L_a$ . The latter condition arises when the specimen has zero power factor.

From the power factor equation (p. 678)  $L_a = L_x + \frac{RF}{p}$ . Hence

$$\begin{aligned} K &= C \frac{R^2 + p^2 L_x^2}{R^2 + p^2 L_x + p L_x R F} \\ &= C \left[ 1 - \frac{p L_x F}{R} \right] \text{ approximately} \end{aligned}$$

If the frequency is 1,000 cycles,  $R$  is 1,000 ohms, and  $F$  is 10 per cent, then  $L_x$  may be as large as 1.5 millihenrys before the correction term is as large as 0.001.

<sup>4</sup> Curtis, Mica Condensers as Standards of Capacity. B. S. Bull. 6, p. 441; 1911 (B. S. Sci. Paper No. 137).

## 2. POWER FACTOR

If an alternating electromotive force is impressed on an air condenser, the current which flows is  $90^\circ$  out of phase with the electromotive force and there is no power loss in the condenser. However, with a condenser having a solid dielectric, the current is not generally  $90^\circ$  out of phase with the electromotive force and there is a loss of

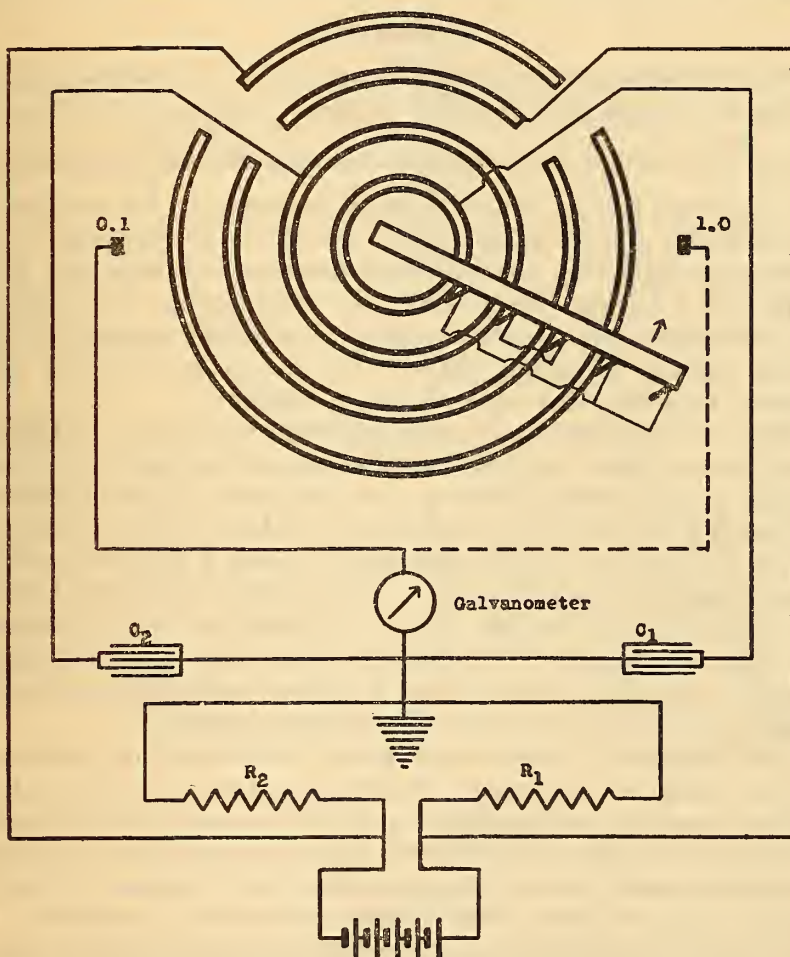


FIG. 4.—Diagram to show the method of measuring capacities by the method of mixtures

The specimen is represented by  $C_1$  and a standard condenser by  $C_2$ . A balance is obtained by varying one of the resistances. Then  $C_1 R_1 = C_2 R_2$ .

power in the dielectric. The equation which gives the power loss is  $P = EIF$ , where  $E$  and  $I$  are the electromotive force and current, respectively, and  $F$  is the power factor. Hence the power factor does not depend on the dimensions of the specimen. It can be determined from electrical measurements alone.



An alternating-current bridge can be used for measuring the power factor. In the Rosa bridge shown in Figure 3, the power loss in the condenser is compensated by means of the variable inductance  $L$ . The value of the power factor <sup>5</sup> is given by the equation

$$F = \frac{p(L_a - L_x)}{R_1}.$$

### 3. RESISTIVITY

The volume resistivity has been determined by measuring the resistance of a specimen of known thickness and area. The formula is  $\rho = \frac{RA}{d}$  where  $\rho$  is the resistivity of the material and  $R$  the resistance of a specimen having an area  $A$  and a thickness  $d$ . On account of the difficulty of eliminating leakage currents in different parts of the measuring apparatus, the resistance measurements were not made with high precision. Hence there was no difficulty in making the thickness and area measurements with sufficient accuracy. The same methods of making these measurements were used as have already been described under dielectric constant.

When an electromotive force is applied to a specimen, a relatively large current flows at first, but this current decreases with time, rapidly at first, then more slowly. An equilibrium condition may not be reached till the electromotive force has been applied for several hours or even days. If the electromotive force is removed, and the electrodes short-circuited, a reverse current will flow for a time which is comparable with the time that was required for the direct current to reach its minimum. If an electromotive force is applied during the time that the reverse current is flowing, this reverse current is added to, or subtracted from, the new direct current.

The resistance of a specimen is defined as the ratio of the electromotive force to the current. From the preceding statement it is evident that the resistance of a specimen increases with increasing time of electrification and depends, to some extent, on the direction, magnitude, and time of the preceding electrifications. The resistance will be definite only as these quantities are specified. In this research, the practice has been followed of first short-circuiting the electrodes till the effect of previous electrifications has become negligibly small. This required from one to three minutes, depending on the specimen. Then an electromotive force was applied and the current read at the end of one minute. While there is some decrease

<sup>5</sup> The complete formula is

$$F = \frac{p(L_a - L_x)}{R_1} \left[ \frac{1}{\sqrt{\left(1 + \frac{p^2 L_x^2}{R^2}\right) \left(1 + \frac{p^2 L_a^2}{R^2}\right)}} \right]$$

where the symbols have the same meaning as in footnote 3. Unless the power loss is very large, the correction factor can be made negligible.

in current after one minute, it is relatively small. Hence the exact time of reading the current is not important so long as at least one minute is allowed to elapse after the application of the electromotive force.

The set-up for measuring the resistance<sup>6</sup> is shown in Figure 5. In measuring a specimen, the switch *AB* is first thrown to *B*. If

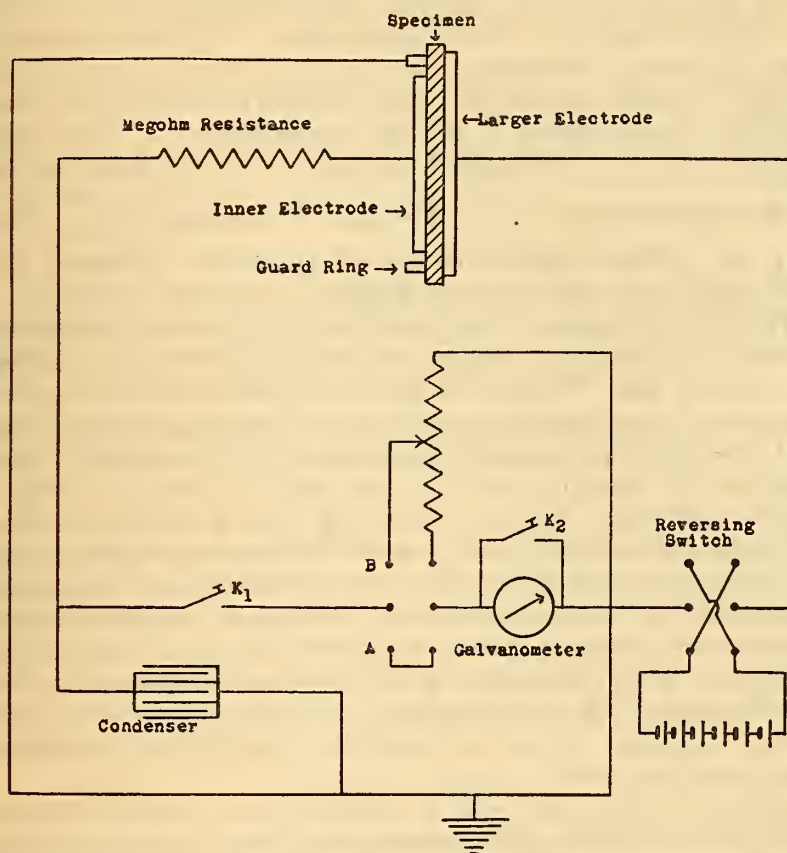


FIG. 5.—Diagram to show the method of measuring high resistances by the galvanometer method

For resistances below  $10^{11}$  ohms, the switch is thrown to *B* and the resistance measured by direct deflection. For higher resistances, the switch is thrown to *A* and a leakage method used.

the current is greater than  $3 \times 10^{-11}$  amperes, a readable deflection will be obtained on a sensitive galvanometer. The resistance is then determined by comparing the current which flows through the specimen from the inner electrode, with that which flows through a standard resistance, the same battery being used in both cases. A universal shunt increases the range of the galvanometer.

<sup>6</sup> Curtis, *Insulating Properties of Solid Dielectrics*. B. S. Bull., 11, p. 362; 1914 (B. S. Sci. Paper No. 234)

If the current is less than  $3 \times 10^{-11}$  amperes, the galvanometer deflection is too small to give a satisfactory measure of the current. However, if the key  $K_1$  is opened, the current will charge the condenser. When the charge is sufficiently large, it can be measured by discharging it through the galvanometer and reading the ballistic deflection. For this use it is well to throw the switch to the position  $A$ , as the removal of the damping resistance appreciably increases the ballistic sensitivity of the galvanometer. The procedure is to close  $K_1$ , thereby discharging the condenser, note the time at which it is again opened, and also the time at which it is a second time closed. With the second closing of the key, the deflection  $D$  of the galvanometer is read. If the applied electromotive force is  $E$  and the time between the opening and the closing of  $K_1$  is  $t$ , then  $R = \frac{Et}{KD}$  where  $K$  is the ballistic constant of the galvanometer. Ordinarily it is undesirable to extend the time  $t$  beyond two or three minutes.

The primary purpose of the guard ring is to prevent current from flowing from the inner electrode to the opposite electrode through any surface film. Without a guard ring, the current which will flow through a submicroscopic film of moisture may be many times that which will flow through the specimen. One can readily appreciate this by recalling that the resistivity of rubber is at least a billion ( $10^9$ ) times that of water. By placing around the inner electrode a guard ring which is kept at the same potential as the inner electrode, only the current which flows through the specimen is measured by the galvanometer. The use of the guard ring is essential when the humidity of the surrounding air is high, since in such a case a film of moisture is deposited on the specimen. With low humidities, this film disappears. Experience shows that, with rubber specimens, the surface resistivity is high if the humidity is less than 50 per cent.<sup>7</sup>

The use of the guard ring is attended with certain difficulties. It is difficult to secure perfect contact at all points between the guard ring and the specimen. At points where the contact is imperfect, current may flow from the inner electrode under the guard ring, thus introducing large errors. Also it is practically impossible to insure that the guard ring is, at all times, at the same potential as the inner electrode. For example, when using the condenser method described above, the potential on the condenser tends to rise, thus introducing a potential difference between the guard ring and inner electrode. This potential difference causes a current to flow which partially discharges the condenser. In this case the allowable resistance between the guard ring and inner electrode is decreased as the capacitance of the condenser is increased. A test of the

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<sup>7</sup>See footnote 6, p. 679.



sufficiency of the resistance between the guard ring and inner electrode is to measure the specimen with two different voltages or with two different times of leakage. If the measured resistance of the specimen is the same under both conditions, the resistance between the guard ring and inner electrode is sufficiently high. An error due to this same cause is introduced in measuring by direct deflection if the potential drop in the galvanometer is sufficient to cause an appreciable current flow between the inner electrode and guard ring.

Another difficulty sometimes arises because of electromotive forces which are produced by electrolytic action at the metallic edges of the guard ring and inner electrode. The inner electrode and guard ring serve as the two electrodes of a primary battery, with the intervening layer of moisture as the electrolyte. This cell may send a current through the galvanometer which is as large or larger than the current through the specimen. To test for this, the galvanometer circuit should be closed with the battery disconnected. Absence of deflection shows that this electromotive force is negligible, at least for direct deflection measurements.

### III. EFFECT OF FREQUENCY, TEMPERATURE, AND PRESSURE ON THE ELECTRICAL CONSTANTS

It has been necessary to measure most of the samples under normal conditions of temperature and pressure, and with alternating current of 1,000 cycles per second. In a submarine cable, the temperatures are low, the pressures high, and the speed of signaling very slow compared to 1,000 cycles. Hence, a few samples have been studied through a range of conditions extending from those at which the measurements were made to those to which the material will be subjected in a submarine cable.

#### 1. EFFECT OF FREQUENCY

Measurements of the dielectric constant have been made with alternating current using both 1,000 cycles and 60 cycles, and with a cyclic direct-current method using both 0.6 second charge and 0.1 second discharge, and 0.6 second charge and 1.0 second discharge. These results, together with measurements of power factor and resistivity, are given in Table 1.

The dielectric constant increases with decreasing frequency in all cases. The maximum change in dielectric constant in the range of frequencies employed was 10 to 15 per cent for crude rubber, gutta-percha, and pure gum compounds. In the case of rubber compounds which contained fillers, a larger change was observed. The compound which contained 20 per cent carbon presented an extreme case with a change of 100 per cent.

The power factor was measured at 1,000 cycles and 60 cycles. The power factor increases with decreasing frequency. Moreover, those samples with low power factor show small change of dielectric constant with frequency, though no quantitative relationship has been shown to exist.

The resistivity of those samples having a low power factor is high. In the table the specimens are arranged in the order of increasing values of 60-cycle power factor. They are also approximately in decreasing order of resistivity. However, the power loss computed from the resistivity is only an inappreciable part of the measured loss.

TABLE 1.—*Change of dielectric constant and power factor with frequency*

Sample number	Dielectric constant				Power factor			Resistivity
	Alternating current		Direct current 0.6 second charge		Maximum increase	1,000 cycles	60 cycles	
	1,000 cycles	60 cycles	0.1 second discharge	1.0 second discharge				
					Per cent	Per cent	Per cent	Ohm-cm
1-----	2.67	2.67	2.86	2.94	10	0.20	0.2	80×10 <sup>14</sup>
2-----	2.62	2.63	2.81	2.87	10	.2	.3	50
3-----	2.82	2.84	3.01	3.07	9	.4	.5	60
4-----	2.38	2.40	2.65	2.70	14	.3	.5	30
5-----	2.89	2.90	3.25	3.32	15	.35	1.2	20
6-----	3.58	3.85	4.15	4.42	24	-----	3.5	.3
7-----	9.76	10.3	11.9	13.1	35	1.9	4.8	.5
8-----	6.12	8.61	10.3	12.4	102	7.5	10.5	.4

*Composition of the above samples*

No. 1	Per cent	No. 5	Per cent
Rubber-----	90¾	Smoked sheet rubber-----	96
Zinc oxide-----	5	Sulphur-----	4
Sulphur-----	4		
Thiuram-----	¼		
No. 2		No. 6	
Gutta-percha from Tjipetir plantation.		Alaskan Cable, 40 per cent rubber insulation.	
No. 3		No. 7	
Refined commercial gutta-percha.		No. 1 with 75 per cent zinc oxide added.	
No. 4		No. 8	
Pale crêpe rubber.		No. 1 with 20 per cent carbon added.	

## 2. EFFECT OF TEMPERATURE

During the early part of the investigation measurements were made on about 20 samples at 5, 20, and 50° C. The results, for the most part, agree with those to be found in the literature. No measure-

ments have been made with the improved samples and the perfected methods of measurement. Hence quantitative data are withheld till such measurements can be made.

### 3. EFFECT OF PRESSURE

A few samples have been measured at pressures up to 10,000 lbs./in.<sup>2</sup> This work is still in progress, and a more complete report will be prepared later. Measurements were made before applying the pressure and again after it was released. Specimens were kept at the higher pressure for several hours. In the computations no allowance was made for the change of dimensions with pressure. The dielectric constant of specimens of gutta-percha and of samples of the old Alaskan cable decreased with increasing pressure. On the other hand, all of the samples of soft rubber prepared in the laboratory showed an increase of about 5 per cent. The one sample of hard rubber showed a barely measurable increase at 10,000 pounds pressure. The results are given in Table 2.

TABLE 2.—*Change of dielectric constant with pressure at 20° C. measured with 1,000 cycles*

Material	Dielectric constant at atmospheric pressure	Increase at 10,000 pounds pressure
Gutta-percha.....	3.23	<i>Per cent</i> —1
Alaskan cable <sup>1</sup> .....	4.39	—2
Low zinc oxide stock.....	3.29	+6
Medium zinc oxide stock.....	3.71	+5
High zinc oxide stock.....	7.10	+6
Asbestine filler.....	4.24	+5
Hard rubber.....	3.50	+0.3

<sup>1</sup> Mean of three samples of recovered cable.

TABLE 3.—*Composition of the samples in Tables 2, 4, and 5*

Name	Percentage of ingredients					
	Rubber	Zinc oxide	Ozokerite	Sulphur	Thiuram	Asbestine
Low zinc oxide stock.....	79.4	10.0	8.0	2.4	0.2	-----
Medium zinc oxide stock.....	71.0	18.0	7.8	3.0	.2	-----
High zinc oxide stock.....	44.0	50.0	4.2	1.7	.1	-----
Asbestine filler.....	41.0	1.5	5.4	2.0	.1	50.0
Hard rubber.....	71.4	-----	-----	28.6	-----	-----

NOTES.—Vulcanization of all specimens except hard rubber was carried out for 15 minutes at 134° C. with a 20-minute rise to bring specimens to vulcanizing temperature.  
Hard rubber specimen was vulcanized six and one-half hours at 142° C.

The power factor increases with increasing pressure. The changes are not very significant, except possibly in the case of gutta-percha where the power factor doubles in going to 10,000 pounds pressure.



The increase for soft rubber samples averages about 10 per cent. Hard rubber shows a slight decrease. Results are given in Table 4.

TABLE 4.—*The change of power factor with pressure at 20° C. measured with 1,000 cycles*

Material	Power factor	
	At atmospheric pressure	At 10,000 pounds pressure
	<i>Per cent</i>	<i>Per cent</i>
Gutta-percha.....	1.0	1.9
Alaskan cable.....	4.0	4.2
Low zinc oxide stock.....	0.4	0.4
Medium zinc oxide stock.....	.6	.7
High zinc oxide stock.....	.9	1.0
Asbestine filler.....	2.1	2.3
Hard rubber.....	.4	.3

The resistivity increases with pressure. With the one sample of gutta-percha which has been measured, the increase was quite marked; the value at 10,000 pounds pressure being eight times as large as at atmospheric pressure. This is larger than accepted values and needs confirmation before being accepted.

TABLE 5.—*Change of resistivity with pressure at 20° C. with one minute electrification*

Material	Resistivity	
	Atmospheric pressure	10,000 pounds pressure
	<i>Ohm-cm</i> $18 \times 10^{14}$	<i>Ohm-cm</i> $140 \times 10^{14}$
Gutta-percha.....	19	5
Alaskan cable.....	2	38
Low zinc oxide stock.....	2.1	2.5
Medium zinc oxide stock.....	19	20
High zinc oxide stock.....	14	18
Asbestine filler.....	110	420
Hard rubber.....		

#### IV. PREPARATION OF SPECIMENS AND THEIR ADAPTATION TO ELECTRICAL MEASUREMENTS

In order to determine the electrical constants of a material it is necessary that specimens be prepared which can be placed between two electrodes, thus forming a condenser. To facilitate the electrical measurements, the distance between the electrodes should be small and their area large, so that the capacitance will be relatively large and the resistance small. In order to compute the dielectric constant and resistivity the sample must be of such a form that the thickness and area can be measured with the same accuracy as the capacitance and resistance. The form of specimens must also be adapted to the methods of manufacture so that specimens which

give uniform and reproducible results can be readily produced through a wide range of materials. Again, the specimen must be of such a form that all moisture can be eliminated, either by drying all materials and carrying on the manufacturing process so that no moisture can enter, or by drying the specimens after manufacture.

No single type of specimen has been devised which completely meets all these requirements. The forms most used were insulated wires, molded sheets, and sheets with embedded electrodes. Each of these has certain advantages. All are still being used for certain measurements.

### 1. INSULATED WIRES

Wires were insulated by the extrusion process. This method of preparation is suitable for only a limited range of insulating materials. Moreover, with such specimens it is difficult to determine with sufficient accuracy the average thickness of the insulation, especially since the wire is seldom accurately centered. However, by using long wires it is possible to get large capacitance and low resistance, both of which are advantageous in making the electrical measurements. For measurements at high hydrostatic pressure this is the only form of specimen which has been used.

### 2. MOLDED SHEETS

A large part of the results reported in this investigation were made on circular molded sheets with raised rims, the form of which is illustrated in Figure 6. These were made in two sizes, 18 cm in diameter and 28 cm in diameter, respectively, the width of the rims being additional. The thickness of the specimens varied somewhat with

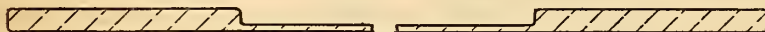


FIG. 6.—Cross section of a molded specimen

the consistency of the stock and the evenness of flow while the sheets were being molded, but, in general, the smaller sheets were about 0.04 cm in thickness and the larger sheets about 0.06 cm. The rims were 2 cm wide and 0.2 cm thick with the small specimens, and 3 cm wide and 0.3 cm thick with the large specimens.

The molding and vulcanizing of the sheets was carried out in one operation by means of a hydraulic vulcanizing press. It was the usual practice to place the requisite amount of the rubber stock in the mold as a lump about  $\frac{1}{2}$  cm thick and to apply hydraulic pressure quickly. Since this operation was done at the temperature of vulcanization, the rubber flowed and filled the mold readily. Much less difficulty was encountered from mechanically entrapped air with this procedure than when the stock was calendered approximately to the thickness of the finished sheet.

The temperature during vulcanization was controlled automatically, and seldom varied more than  $\frac{1}{2}^{\circ}$  C. Measurements with thermocouples indicated that there was no substantial difference between steam temperature and the temperature of the specimen during vulcanization. When molds were removed from the press to take out specimens and put in fresh stock, some cooling was unavoidable. This amounted to as much as 5 to  $8^{\circ}$  C. when the temperature was  $150^{\circ}$  C., and three to four minutes were required to regain the indicated temperature. Except with very short cures, this amount of lag is negligible.

Molds made from cold-rolled aluminum were used in preparing most of the specimens for this investigation. These were found to have distinct advantages over iron molds, which were used at first. Both the time of heating and the temperature lag were less than for iron molds, but this was probably due to the fact that the surface of the aluminum was polished and that of the iron was oxidized rather than to the superior thermal conductivity of the aluminum.

A soap solution was applied to the surface of the iron mold to prevent the rubber from sticking. It was found that this soap solution caused overcuring at the surface. This prevented the production of uniform samples, which was especially noticeable in the thin specimens used in this investigation. This difficulty was completely obviated by the use of aluminum molds, to which the rubber does not stick.

As has been pointed out elsewhere in this discussion, moisture induces wide variations in the electrical properties of rubber and must be carefully eliminated before measurements are made. In the preparation of molded sheets, the mixing and vulcanizing was carried out in the usual way without particular precautions, and reliance was placed on desiccation of the sheets after they were made. This desiccation was done by keeping the sheets in a closed metal chamber over concentrated sulphuric acid for a drying agent for a period of three days or longer at  $30^{\circ}$  C. A fan was used to secure rapid circulation of dry air.

No simple method of applying metal electrodes to molded sheets has been found. If the specimen is placed between flat plates, air films always remain, which materially influence the results of electrical measurements. For all the measurements here reported, water electrodes have been used. These have the disadvantage that water may be absorbed by the specimen, thus changing the measured values. As the water absorption is relatively slow, this difficulty may be avoided by making the measurements as rapidly as possible after the electrodes are applied.



In order easily to use water electrodes with sheet specimens, two special holders were constructed to take the two sizes of specimens described above. All of the features are contained in the larger one,

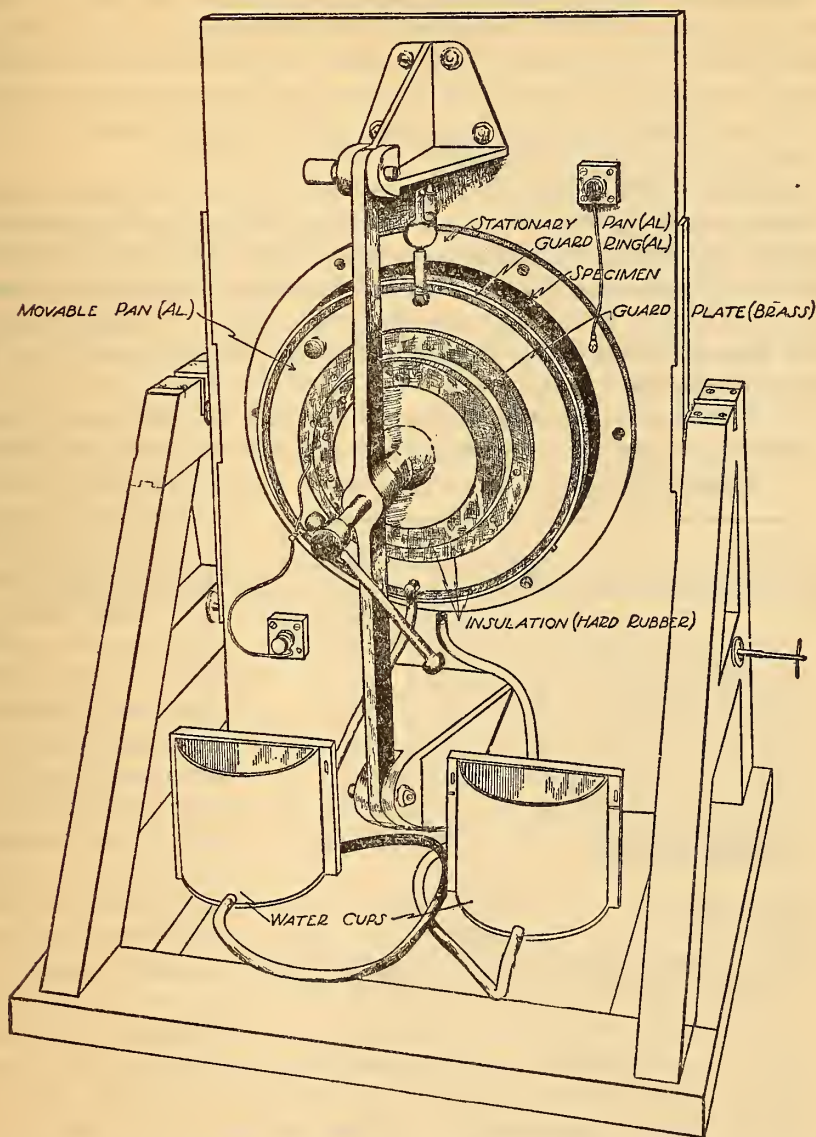


FIG. 7.—Holder for the molded specimens

The specimen is clamped between the holders and the water cups are raised to bring the water on both sides of the specimen

a sketch of which is shown in Figure 7. The specimen can be clamped at the edges between aluminum holders in the form of recessed plates which are like very shallow pans with heavy sides and thick bottoms.

To one side of each pan there is attached a rubber tube connecting to a cup containing water.

In using the apparatus the cups are lowered, the pans brought to a horizontal position, the specimen inserted and clamped. Then the whole apparatus is turned so that the specimen is vertical with the rubber tubes attached at the bottom. The cups are then raised, filling the pans with water from the bottom. In this way the air is swept out ahead of the rising water, so that a good contact is made between the water and sample.

A guard ring is provided to decrease surface leakage when making direct-current measurements. The guard ring is not designed to modify appreciably the electrostatic field at the edge of the specimen. For this purpose the gap between the guard ring and electrode must be small relative to the thickness of the specimen. To make the gap this narrow would decrease greatly the effect of the guard ring in preventing surface leakage.

If thin sheet specimens without the raised rims are used in the holder, the edges are compressed a considerable amount, so that a

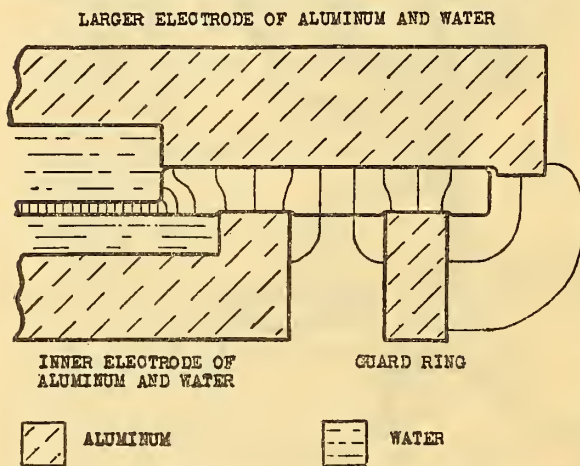


FIG. 8.—Diagrammatic cross section of edge of molded specimen and holder showing lines of force between the electrodes.

Lines of force indicated by thin, solid lines.

rather large error is introduced. To minimize this, the molded specimens have been made with a thick rim around the edge, as previously described. This has the disadvantage of distorting the electrostatic field in this region. A drawing showing, in a qualitative way, the distribution of the electrostatic lines of force is given in Figure 8. The edge effects are complicated and not completely calculable. As a first approximation, the assumption has been made that the lines of force are always perpendicular to the surface of the inner electrode. However, this gives a value of the computed capacitance which is too small, making the dielectric constant too large. This is shown by the fact that with specimens having as near as possible the same properties, those measured in the smaller holder in which the edge is large relative to the area, had the largest dielectric constant; those measured in the larger holder had an inter-

rather large error is introduced. To minimize this, the molded specimens have been made with a thick rim around the edge, as previously described. This has the disadvantage of distorting the electrostatic field in this region. A drawing showing, in a qualitative way, the distribution of the electrostatic lines of force is given in Figure 8. The edge

mediate value of the dielectric constant, while those measured with embedded electrodes (described later) had the smallest value of the dielectric constant. Factors which were determined experimentally have been used to reduce all the measurements to the same basis. Considerable more research will be required to ensure that this basis is the correct one, but the error in the present values probably does not exceed a few per cent.

### 3. SPECIMENS WITH EMBEDDED ELECTRODES

The specimens with embedded electrodes as shown in Figure 9 were first developed for crude rubber. They served the purpose so well that their use was extended to gutta-percha and vulcanized rubber. They have some advantages over any of the other types of specimens.

In making these specimens the requisite amount of stock, usually in the form of a round lump 1 to 2 cm thick, was placed between thin disks cut from cold-rolled aluminum, and a sheet was formed by subjecting this "sandwich" to hydraulic pressure between the platens of a vulcanizing press. If the material were crude rubber

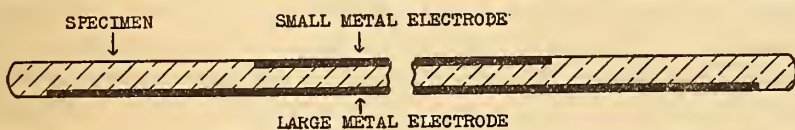


FIG. 9.—Cross section of specimen with embedded electrodes

or gutta-percha a temperature of 80 or 90° C. was employed, but if a vulcanized specimen were desired the sheet was formed and vulcanization was carried out at the requisite temperature. To avoid the necessity of accurately centering the disks, one was made larger than the other. The majority of the specimens have been made with disks 22 and 24 cm in diameter. The over-all thickness, which was about 1 or 1½ mm, was determined by a copper ring of the desired thickness which surrounded the specimen and kept the platens at this distance apart. Sheets of paraffined paper placed between the platens and the specimen prevented the rubber which flowed out around the aluminum disks from adhering to the platens. The paper usually adhered to the 1 cm rim of rubber around the edge of the condenser, but this was in no way objectionable.

While specimens with embedded electrodes could not be examined visually before testing, they were frequently taken apart after measurement. Except in case of some hard-rubber specimens no defects were encountered. There were seldom any entrapped air bubbles, and in no case enough to vitiate the results. The rubber made perfect contact with the metal without any intervening film of air.



When rubber is thus molded between metal plates, it is not possible to effect drying after the specimens have been prepared. Consequently, dry materials must be used in the preparation. It was found that the hot milling of rubber in small batches was adequate for removing small amounts of moisture. The compounding ingredients were dried before use, and the stock was stored in a desiccator until specimens were prepared. The power-factor values, which are very sensitive to traces of moisture in rubber, indicated that more uniform and satisfactory desiccation was attained with these specimens than with sheets which were dried after preparation.

The advantages and disadvantages of the different types of specimens can be summarized as follows: Insulated wires can be used to give a large capacitance and low resistance, which can be measured by simply immersing the specimen in water. However, only a limited number of materials can be applied to wires, and even with these the thickness can not be accurately measured since the wire is not perfectly centered. Insulated wires are valuable for relative measurements only. Molded sheets can be carefully examined, thoroughly dried, and their dimensions accurately measured. However, their use requires water electrodes which are undesirable. Moreover, they must be held in a large, cumbersome apparatus, especially designed for this purpose. Specimens with embedded electrodes can readily be prepared from a wide range of materials, their dimensions can be accurately measured, and they are in excellent form for the electrical measurements. However, they must be prepared from carefully dried material since moisture can not be eliminated after the specimen is prepared. Also, the specimen can not be examined until all measurements on it have been completed.

## V. COMPOSITION AND PREPARATION OF GUTTA-PERCHA AND RUBBER<sup>8</sup>

Neither rubber nor gutta-percha are ordinarily employed for purposes of electrical insulation in the form in which they come to market. The treatment of gutta-percha aside from mechanical purification by washing is chiefly concerned with the blending of

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<sup>8</sup> The purpose of this section is to acquaint the reader who is not familiar with rubber and gutta-percha with the source, composition, and means of preparing these materials for use. This is done to give a better understanding of the discussion of electrical properties which will follow. For further information the reader is referred to the many books on gutta-percha and rubber. A few books of general interest are listed below:

Die Guttapercha, Obach; 1899.

India Rubber and Gutta-Percha, Seeligman, Torrilhon, and Falconnet; translated by McIntosh; 1910.

The Gutta-Percha and Rubber of the Philippine Islands, Sherman, Report of Philippine Commission, No. 7; 1903.

The Preparation of Plantation Rubber, Morgan and Stevens; 1922.

Systematic Survey of Rubber Chemistry, Bedford and Winkelman; 1923.

The Testing of Rubber Goods, B. S. Circular No. 38; 1921.

The Chemistry of Rubber, Luff; 1923.

different varieties and kinds so as to obtain the desired mechanical and electrical properties. Rubber, on the other hand, is generally vulcanized and may be compounded with a wide variety of materials.

### 1. GUTTA-PERCHA

Gutta-percha is a gum which is obtained by the coagulation of the milk or latex of certain tropical trees belonging to the order *Sapotaceæ*. Gutta-percha is hard and tenacious at ordinary temperatures and becomes plastic and capable of being molded when it is warmed to about 50° C. Gutta-percha is made up of two main components—gutta, to which it owes its characteristic properties, and resinous materials. The gutta may comprise from 20 to more than 90 per cent of the composition, depending on the source and mode of preparation of the gum. Gutta is a hydrocarbon having the empirical formula  $(C_5H_8)_n$ , but it is not identical with the rubber hydrocarbon which has the same empirical formula.

The highest possible gutta content is by no means desirable in gutta-percha that is to be used for submarine-cable insulation or for similar purposes. A certain proportion of the resins is necessary to render the material workable and to impart the desired mechanical properties. The processes which are used in the manufacture of gutta-percha products consist in the selection of different varieties of the gum and blending them so that the desired composition and physical properties are obtained. Small quantities of other materials, such as paraffin, ozokerite, and gutta balata are frequently added. Since most of the gutta-percha on the market<sup>o</sup> is collected and prepared by native methods, the raw material is not constant in composition or quality, so an element of experience and judgment enters into the manufacturing process. Manufacturers using gutta-percha keep most of their accumulated information as trade secrets.

### 2. CRUDE RUBBER

Crude rubber, india rubber, or caoutchouc is an elastic gum produced by a wide variety of plants, including herbs, shrubs, vines, and trees. However, the greater part of the rubber of commerce comes from the tropical tree *Hevea brasiliensis*. Rubber can also be prepared by chemical synthesis. Rubber exists in a plant as microscopic globules in the milk or latex of the plant. When it has been separated from the latex it is known to the trade as crude rubber. The term crude does not refer to the state of purity, but is used to distinguish the product in its natural state from the rubber of commerce, which is generally a chemical compound of crude rubber and sulphur.

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<sup>o</sup> Plantation gutta-percha is on the market, but the production is still only a fraction of the production of the wild gutta-percha.

There are a number of varieties of crude rubber, depending on the source and method of preparation. Smoked sheet, pale crêpe, and latex-sprayed rubber are all produced from plantations of Hevea trees in the Far East. In the preparation of smoked sheet, the latex is coagulated by the addition of 1 part of acetic acid to 1,000 parts of latex. The coagulum is washed and sheeted. The sheets are then dried and smoked. The smoking is especially for preventing the growth of molds. The preparation of pale crêpe differs in that sodium bisulphite, as well as acetic acid, is added to the latex before coagulation. Also, more thorough washing is given to remove constituents which would promote mold growth, and the product is made in the form of thin, crinkled sheets from which the name, crêpe, is derived. The latex-sprayed rubber is made in this country from preserved latex. The process consists in passing a current of dry air through a spray of latex, removing all the volatile materials, and leaving behind all the nonvolatile constituents, including some natural preservatives of the rubber. Para rubber is prepared by crude methods of smoking and drying the latex of Hevea trees found in the forests of the upper Amazon. Cameta is an inferior type of Para. Gayule is produced from a Mexican shrub.

Crude rubber is chiefly rubber hydrocarbon, the composition of which may be expressed by the empirical formula  $(C_5H_8)_n$ . In addition to the hydrocarbon, crude rubber contains small amounts of resins, proteins, sugars, and mineral salts derived from the original latex, and other constituents present in consequence of the method of preparation of the particular variety of rubber. In plantation smoked-sheet and fine Para rubber are small amounts of constituents taken up from smoke, while pale crêpe rubber contains traces of sodium bisulphite added to preserve the characteristic light yellow color. The latex-sprayed rubber contains all the solid constituent of the original latex. The substances other than rubber hydrocarbon are not to be regarded as impurities, but rather as accessory components, since they have a marked effect on its properties. The removal of the resins, for example, gives a rubber which is not only difficult to vulcanize, but one which ages rapidly in service.

### 3. VULCANIZED RUBBER

Vulcanized or cured rubber is a chemical combination of crude rubber and some other substance, usually sulphur. It may be produced by mixing rubber and sulphur and heating for some time. If the amount of sulphur and the time and temperature of heating have been properly chosen, the resulting vulcanized rubber retains its elastic properties over a considerably greater range of temperature than does crude rubber. While methods of curing rubber without the



use of heat are known, they have not been employed in this investigation.

Four more or less distinct processes may be involved in the making of a rubber article from crude rubber: (1) The crude rubber is washed to remove mechanical impurities, then sheeted and dried. (2) The dried sheets are milled and mixed with sulphur and other compounding ingredients to form a stock compound. (3) The stock is then sheeted, tubed, or otherwise processed to give it the form desired in the finished article; and (4) the article is vulcanized. With uniform, high-quality plantation rubber, the first step, that of washing, is frequently omitted. The third and fourth steps are combined when molded articles are made since molding and vulcanization are carried out in one operation.

Crude rubber frequently contains dirt, bark, splinters from packing cases, and various other foreign materials. These foreign materials are readily removed by washing the rubber with jets of water while it is subjected to mechanical working between corrugated rolls. This washing also eliminates some of the water-soluble impurities, but their complete elimination requires a much longer treatment than for removing foreign materials. The drying of rubber, after it has been washed, is accomplished either by hanging it in warm darkened rooms for several weeks or by the use of a vacuum dryer at an elevated temperature.

Before compounding ingredients can be mixed with rubber it must first be plasticized, or "broken down" on a rubber mill. This is accomplished by the combined action of mechanical working and heat, which change the rubber into a plastic material with which powders and waxes may be mixed. Temperature regulation is a very important consideration in the process of mixing rubber, because too high a temperature causes premature vulcanization. The poor thermal conductivity of rubber renders the accurate control of the temperature a matter of difficulty. In practice, temperature regulation is more a matter of skill and judgment than scientific control. The warm plastic rubber stock is processed to give the form desired for the finished article. If sheets are wanted these are obtained by passing the stock between heated calender rolls. Tubing is formed by extruding the stock through an annular opening. Insulation may be applied to wire either by an extrusion process, which gives a seamless covering, or by wrapping the stock around the conductor in the form of tape.

There are two general means of hot vulcanization. Many articles are vulcanized by placing them in steam at a definite pressure. Sheets and objects which can be molded are formed and vulcanized by a single operation in a hydraulic press having steam-heated platens.

In either case the temperature may be controlled automatically by controlling the steam pressure.

Vulcanization, like chemical reactions in general, has a large temperature coefficient, so that increasing the temperature decreases the time required. Since a change of  $10^{\circ}$  C. in the temperature of vulcanization is roughly equivalent to a change of 100 per cent in the time, accurate control of temperature is necessary. The particular temperature selected depends on the composition of the stock. Temperatures of  $160$  or  $170^{\circ}$  C. are generally used for hard rubber and  $125$  to  $145^{\circ}$  C. for soft rubber.

When a number of specimens of the same composition are vulcanized for different lengths of time at a given temperature they show a progressive change in physical properties with time of vulcanization. Specimens which have been vulcanized for a short time are tacky and lacking in strength. They are called undercured. Those which have been vulcanized a long time are stiff, easily torn, and lacking in strength. They are called overcured. At some intermediate time of cure the specimens have the maximum strength. Such specimens are said to have received the optimum cure. The time for optimum cure is generally determined experimentally for each kind of stock. The ultimate tensile strength of a series of specimens which have been vulcanized for different lengths of time is measured. By plotting tensile strength against time of vulcanization a curve is obtained from which the time of vulcanization for optimum cure can be read. Sometimes this curve has a sharp peak, indicating that optimum cure can only be obtained within narrow time limits. With other compounds the curve has a flat portion in the center. Such compounds are said to have a flat cure.

#### (a) ACCELERATORS

Early in the history of the rubber industry it was discovered that litharge, lime, magnesia, and other inorganic bases accelerated the reaction of rubber and sulphur, enabling vulcanization to be conducted more quickly than in their absence. In recent years aniline and other organic bases were found to have similar action, and the list was soon extended to include a great variety of organic compounds, many of them nonbasic in nature. Accelerators now comprise such a wide variety of substances that almost the only characteristic which they have in common is the fact that they increase the rate of reaction of rubber and sulphur. There is some indication that rubber and sulphur would not react if it were not for certain natural accelerators in the crude rubber.

The function of accelerators is much more far-reaching than that of a catalyst which modifies the rate of a reaction. The amount of sulphur required to give a product of the best physical properties is

much less when an accelerator is used than when vulcanization is effected with sulphur alone. Moreover, with the aid of an accelerator, a product can frequently be obtained which has superior mechanical properties to any that can be produced by the use of sulphur alone. A fraction of a per cent of an organic accelerator may increase the tensile strength of rubber by 50 or even 100 per cent, as well as decreasing the time required for vulcanization to a small fraction of its former value.

Some accelerators are of particular value in that they give a "flat" cure. For example, compounds containing certain xanthates and thiuram disulphides often show good physical properties whether they are vulcanized for a few minutes or several hours. For this reason vulcanized-rubber articles made by the use of accelerators are much more uniform than are those made without accelerators. Also rubber which is cured with an accelerator usually shows exceptionally good aging characteristics. There are probably several factors which cause this improved aging. One of the most important is the fact that rubber at its optimum cure oxidizes more slowly than overcured or undercured rubber. Hence an accelerated rubber compound, in which the cure is almost sure to be correct, is much more likely to age well than an unaccelerated rubber, in which the chance of getting correct cure is small.

There is great variability in the amount of natural accelerators in crude rubber. Hence with rubber-sulphur mixtures the time of vulcanization at a given temperature varies greatly with different samples of crude rubber. By the addition of an accelerator this variability can be almost entirely eliminated, since the natural accelerator then plays an insignificant part in the vulcanization process.

#### (b) FILLERS

Pure gum compounds—that is, compounds containing only rubber and sulphur, or rubber, sulphur, and accelerator—find limited application in the manufacture of rubber articles. Fillers in the form of finely divided powders, such as gas carbon, zinc oxide, clay, or whiting, are employed in nearly all types of manufactured rubber goods. They are inert in that they enter into no chemical reaction with the rubber and do not affect the process of vulcanization.

Fillers are frequently used for the purpose of increasing the bulk and decreasing the cost of a rubber compound, but this is by no means their only function. Fillers give a desirable consistency to unvulcanized rubber, thus facilitating the manufacture of rubber goods. Certain fillers impart strength and toughness to rubber and consequently find important application in the manufacture of rubber articles which are subject to mechanical wear.



Soft-rubber insulation generally contains a large proportion of filler. The insulation on wires and cables frequently has as much as 70 per cent of filler and seldom has less than 50 per cent. Hard rubber, on the other hand, usually contains only a small proportion of filler, and in many cases no filler at all.

#### (c) SOFTENERS

In order to facilitate the mixing and processing of rubber stocks another group of compounding ingredients called softeners are employed to render the unvulcanized mixture soft, plastic, and easily worked. Inasmuch as this action is physical rather than chemical, a wide variety of ingredients may be employed for this purpose, including paraffin, waxes, oils, fats, asphaltic and bituminous materials. The amount of softener used depends on the specific nature of the material, and varies from 2 or 3 per cent in the case of paraffin to 15 or 20 per cent in the case of "mineral rubber," which is an asphaltic residue. In the latter case the relative volume of the mineral rubber is such that it might be considered a filler as well as a softener.

### VI. ELECTRICAL PROPERTIES OF CRUDE RUBBER

Measurement of the dielectric constant, power factor, and resistivity were made on a number of samples of the common varieties of crude rubber, with the result that only slight differences in these electrical constants were found between the various high-grade crude rubbers. This is in accord with the fact that the chief component of all the crude rubbers is the rubber hydrocarbon, small amounts of accessory constituents being responsible for the characteristic differences.

The samples of crude rubber were of the usual commercial grades from stock, except the smoked sheet, which was from a bale received fresh from the plantation through the courtesy of the General Rubber Co. Information was given that this smoked sheet had been prepared by the usual plantation process from latex collected some time in January, 1924. The rubber was received and the first tests were made in April, 1924, about two months after the smoking of the rubber had been finished.

As shown in Table 6, the dielectric constant of both the fine Para and the pale crêpe rubbers was 2.43, while that of the smoked sheet as received was 2.53. When measurements on the smoked sheet were repeated after a year, the value 2.38 was obtained. More measurements are needed to establish this change of dielectric constant with time. The average values for the power factor of the three kinds of rubber ranged from 0.15 to 0.19 per cent, though single specimens were found with values as low as 0.09 per cent. The

resistivity values show considerable variation. This may not be entirely due to variations in the specimens, since they were measured at different temperatures. Also the measurements here recorded were made without the use of a guard ring, although precautions were taken to keep the humidity of surrounding air below 50 per cent relative humidity. The error due to the lack of guard ring does not affect the order of magnitude of the resistivity, but it does prevent a comparison of the resistivities of the different rubbers.

The kinds of crude rubber which contain a larger proportion of nonhydrocarbon components, such as sprayed latex rubber and guayule, have somewhat larger values of the dielectric constant and power factor than the commercial high-grade crude rubbers. No significant difference in resistivity values is apparent.

TABLE 6.—*The dielectric constant, power factor, and resistivity of crude rubber*

Kind of rubber	Age (months)	Number of specimens	Dielectric constant at 1,000 cycles	Power factor at 1,000 cycles	Resistivity
Fine Para.....	Unknown.....	13	2.43	<i>Per cent</i>	<i>Ohm-cm.</i>
Pale crêpe.....	do.....	6	2.43	0.14	$35 \times 10^{14}$
Smoked sheet.....	do.....	6	2.53	.16	50
Hopkinson sprayed latex.....	13.....	6	2.53	.19	3
Cameta.....	15.....	3	2.38	.16	10
Guayule.....	Unknown.....	5	2.56	.28	10
Smoked sheet, thoroughly washed and dried.....	do.....	2	2.69	.51	60
Pale crêpe, thoroughly washed and dried.....	do.....	1	2.70	4.0	2
Obach's "pure unvulcanized rubber" <sup>1</sup> .....	12.....	3	2.35	.29	60
Fleming & Dyke's "pure rubber" <sup>3</sup> .....	Unknown.....	3	2.36	.29	40
	do.....		<sup>2</sup> 2.50	-----	28
	do.....		2.60	.5	-----

<sup>1</sup> Obach: *Die Gutta-percha*, p. 72; 1899.<sup>2</sup> Frequency not stated.<sup>3</sup> *J. Inst. El. Eng.*, 49, p. 323; 1912.

The increased value of the dielectric constant, which is associated with the presence of nonhydrocarbon constituents, indicates that the pure rubber hydrocarbon has a relatively low dielectric constant, which is increased by the presence of the accessory components that go to make up the natural rubbers. This is further evidenced by the slight decrease in the dielectric constant which may be brought about through washing of the crude rubber and the consequent removal of part of the water-soluble components. The dielectric constants of pale crêpe and smoked sheet are lowered by thorough washing and become practically identical. The apparent increase of the power factor from about 0.16 to 0.29 per cent by washing is probably due to increased proportion of resins, since the crude rubber was dried in air for several weeks after washing. The resistivity of pale crêpe was not changed appreciably by washing, but that of smoked sheet rubber was increased from less than  $10 \times 10^{14}$  ohm-cm to  $60 \times 10^{14}$  ohm-cm, the latter value being comparable to that which was obtained for other varieties of rubber.

Measurements of the electrical constants of crude rubber have been made by several previous investigators, but apparently little attention has been paid to the source and kind of rubber used or to means for making it into a form suitable for electrical testing. The results which were obtained by two investigators are cited in Table 6. The agreement with our own determinations is fairly good.

## VII. RELATIONSHIP BETWEEN THE DIELECTRIC CONSTANT AND THE REFRACTIVE INDEX OF CRUDE RUBBER

According to the electromagnetic theory of light, the dielectric constant  $k$  of transparent substances is connected with the refractive index  $n$  by the relation

$$k = n^2$$

The agreement between the observed values of the dielectric constant and values calculated from the refractive index is good in case both measurements are made at the same frequency. However, the normal values of both  $k$  and  $n$  decrease with increasing frequency. With many materials the change is small, so that  $k$  measured at telephone or radio frequencies is but little larger than  $n^2$  measured at the frequency of visible light. Rubber is in this class, so as a practical consideration  $n^2$  may be taken as representing the limiting lower value of the dielectric constant.

The refractive index of rubber was measured by means of an ordinary prism refractometer, compensated so that readings were in terms of the  $D$  line when white light was used. The rubber, which had been thoroughly milled, was pressed against the prism in the form of a thin sheet, so as to make optical contact with the glass, without the use of a liquid. The results of the measurements are given in the following table:

TABLE 7.—*Refractive index of crude rubber*

Kind of crude rubber	$n_D$ at 25° C.
Pale crêpe.....	1.519
Smoked sheet.....	1.519
Fine Para.....	1.520
Washed smoked sheet.....	1.519
Washed pale crêpe.....	1.519

It is significant that the various kinds of crude rubber show practically identical values for the refractive index and that no appreciable change is effected by thorough washing. Apparently the refractive index is a function of the rubber hydrocarbon, and is only slightly sensitive to variations in the accessory components of crude rubber. On this basis it is not to be expected that the refractive index of rubber hydrocarbon differs materially from that of crude rubber.



The square of the refractive index of crude rubber is 2.307, which may be taken as approximately the limiting lower value for the dielectric constant. Thoroughly washed crude rubber approached this value, having a dielectric constant of 2.35. It is not to be expected that further purification of rubber or the investigation of other types of crude rubber will lead to a material with a dielectric constant markedly lower than that which had already been obtained.

### VIII. ELECTRICAL PROPERTIES OF GUTTA-PERCHA

There is a much wider variation in the electrical properties of different kinds of gutta-percha than in the electrical properties of different kinds of crude rubber because of the much greater divergence in composition between various kinds of gutta-percha. Gutta-percha may contain from 20 to more than 90 per cent of the characteristic component, gutta, while the remainder of the material is made up of resins, traces of other organic constituents, and mechanical impurities, such as bark and dirt.

No attempt has been made to determine the electrical properties of a great many kinds of gutta-percha. Measurements have been made on two grades of gutta-percha from stock, and on occasional samples from other sources, such as leaf gutta-percha from the Dutch Plantations at Tjipetir. The results have been coordinated with especial reference to showing the effect of resin and moisture on the electrical constants of gutta-percha.

With dry gutta-percha, both the dielectric constants and the power factor increase as the resin content increases, as shown by the curves in Figure 10, which are plotted from results given in Table 8. The constituents other than resin and gutta are left out of consideration. As is noted in the table, the values for 100 per cent resin are those found by Obach.

The presence of moisture in gutta-percha is accompanied by an increase in the dielectric constant and the power loss. This effect is

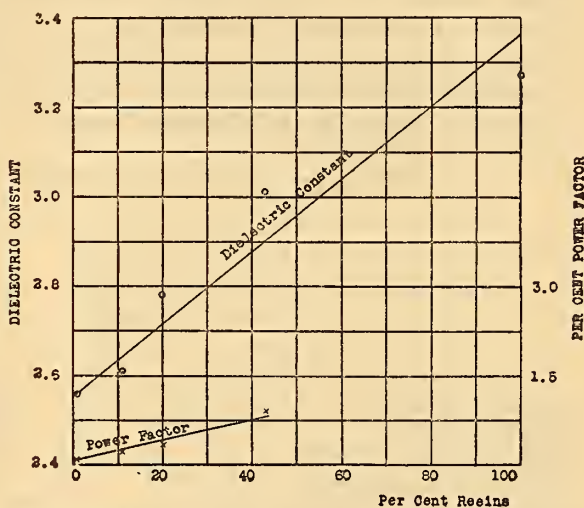


FIG. 10.—Effect of composition on the dielectric constant and power factor of gutta-percha

of primary importance because gutta-percha is usually kept under water to prevent its deterioration from atmospheric oxidation, and commonly contains from 2 to 6 per cent of water. Specimens having embedded electrodes were prepared from gutta-percha which had been stored under water. Some specimens were prepared after wiping off surface moisture from the gutta-percha and duplicate specimens were made after drying the gutta-percha to constant weight in a desiccator. From the results of the tests, which are given in Table 8, it may be noted that the removal of 2.5 per cent of water was accompanied by a decrease in the dielectric constant from 4.13 to 3.01 and a decrease in the power factor from 3.1 to 1.8 per cent. When air-dry Tjipetir gutta-percha was subjected to hot milling to remove the last traces of moisture the power factor was reduced very materially, though the dielectric constant was not changed. Gutta-percha behaves like rubber, in that a small amount of moisture causes a large change in the power factor and a small but appreciable change in the dielectric constant.

TABLE 8.—*The electrical properties of gutta-percha*

Specimen	Composition on dry basis			Water	Dielectric constant at 1,000 cycles	Power factor at 1,000 cycles	Resistivity
	Gutta	Resin	Mechanical impurities				
	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>		<i>Per cent</i>	<i>Ohm-cm</i>
Commercial gutta-percha.....	57.3	39.2	3.5	2.5	4.13	3.1	-----
Commercial gutta-percha, dried.....	57.3	39.2	3.5	0.0	3.01	1.8	25×10 <sup>14</sup>
Refined gutta-percha.....	79.9	19.3	.8	0.0	2.78	.35	60
Refined gutta-percha, extracted with acetone.....	99.0	-----	1.0	0.0	2.56	.09	370
Gutta-percha from Tjipetir Plantation.....	89.2	9.3	1.5	Present.	2.60	1.1	65
Gutta-percha from Tjipetir Plantation, dried.....	89.2	9.3	1.5	0.0	2.61	.23	45
Resin extracted from gutta-percha <sup>1</sup> .....	-----	100	-----	-----	3.27	-----	25
Commercial balata (sheet).....	44.8	39.8	15.4	-----	3.48	2.3	-----

<sup>1</sup> E. Obach, *Die Gutta-percha*, p. 72; 1899.

The dielectric constant which was obtained for the purest gutta-percha that was examined was 2.56. This is about 0.2 of a unit higher than the dielectric constant of the purest crude rubber. This approximate equality of the dielectric constant is to be expected from the similarity in the chemical composition of pure rubber hydrocarbon and pure gutta hydrocarbon. Perhaps this also explains the fact that the lowest value obtained for the power factor of gutta-percha was 0.09 per cent which is the same as the lowest value obtained for a sample of rubber.

A number of values for the dielectric constant and the resistivity of gutta-percha are given in the literature. More attention seems to have been paid to the values for the different kinds of commercial

gutta-percha than to correlation of the electrical properties with the composition. In so far as the materials on which measurements have been made are similar, there is fair agreement between our results and those given by previous investigators.

### IX. ELECTRICAL PROPERTIES OF RUBBER-SULPHUR COMPOUNDS

It would be of interest to study the electrical properties of rubber-sulphur compounds over the whole range in which combination of rubber and sulphur takes place. Up to the present, however, data have been obtained on only two compounds:

		Per cent
First compound--	{Smoked sheet rubber-----	96
	{Sulphur-----	4
Second compound	{Smoked sheet rubber-----	92
	{Sulphur-----	8

The first compound was chosen because 4 per cent of sulphur is near the lower limit with which vulcanized rubber of good physical properties may be obtained in reasonable time. It also forms the

basis for comparison which will be made in another section between accelerated and non-accelerated vulcanization. The compound containing 8 per cent of sulphur is one which is used frequently in the testing of crude rubber, and represents about the proportion of sulphur requisite for best physical properties if vulcanization is to be effected with sulphur alone.

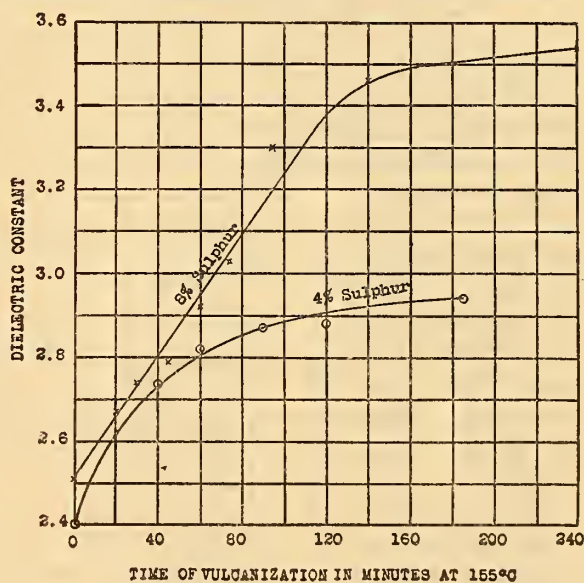


FIG. 11.—Effect of time of vulcanization on the dielectric constant of rubber-sulphur compounds

The effect of vulcanization with sulphur is to increase the dielectric constant and power factor of rubber. The resistivity of rubber apparently is not altered by combination with sulphur. The curves in Figures 11 and 12, which are plotted from data in Table 9, indicate the variation of the dielectric constant and power factor with time of vulcanization for specimens containing 4 and 8 per cent sulphur,



respectively. In both cases the dielectric constant increases with the time and reaches an approximately constant value on long overcuring. The dielectric constant values with 8 per cent sulphur are uniformly higher than those with 4 per cent sulphur. There is no inflection in the curves which might be related to the point of maximum tensile strength.

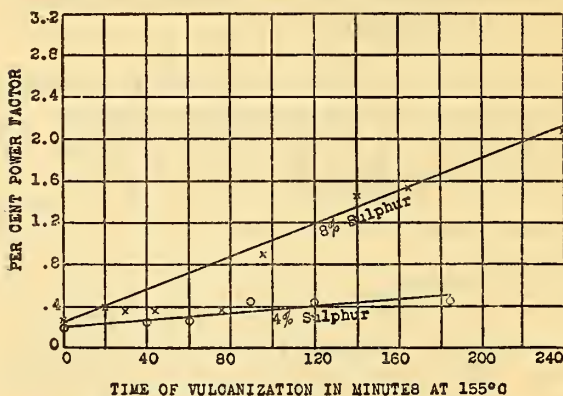


FIG. 12.—Effect of time of vulcanization on the power factor of rubber-sulphur compounds

Values of the power factor are given in Table 9 and plotted in Figure 12. There is apparently a continuous increase in power factor with time of vulcanization, which is more marked for 8 per cent sulphur than for 4 per cent sulphur. The resistivity values are almost all between  $10$  and  $50 \times 10^{14}$  ohm-cm. Any variation in resistivity due to difference in per cent of sulphur or to difference in time or temperature of vulcanization is overshadowed by individual variations between different specimens. The resistivity values for the specimens containing 4 per cent sulphur are more consistent than the others because they were all prepared at the same time and measured under the same circumstances.

Specimens of the compound containing 8 per cent of sulphur were made over a range of cures at the temperatures, 149, 155, and 160° C., to ascertain the effect of time and temperature of vulcanization on the electrical constants. In Figure

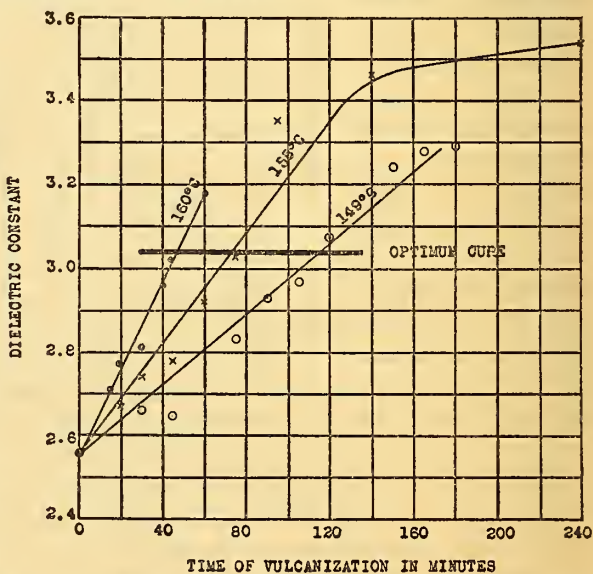


FIG. 13.—Effect of time and temperature of vulcanization on the dielectric constant of rubber-sulphur compounds

Figure 13 the dielectric constant is shown as a function of the time

of vulcanization, at the three temperatures, and the time of vulcanization for the best physical properties is indicated for each temperature. Within the range of temperatures considered, the dielectric constant at the optimum cure is independent of the particular time and temperature used, and dependent only on the state of cure. The values of the power factor are about the same at comparable states of cure for specimens vulcanized at the different temperatures. Variations due to differences in the individual specimens keep the power factor values from showing an even and uniform variation with time of vulcanization.

The simplest interpretation of the change of electrical properties on vulcanization is that the reaction of rubber and sulphur gives rise to a product which has a higher dielectric constant and power factor than a mixture of them alone. For the compounds investigated, factors which increase the proportion of sulphur in combination with the rubber also increase the values of the dielectric constant and the power factor. This has been illustrated by the foregoing results, both as to the effect of increasing the percentage of sulphur and lengthening the time of vulcanization or raising the temperature.

TABLE 9.—*The electrical properties of rubber-sulphur compounds*

Composition	Vulcanization		Dielectric constant at 1,000 cycles	Power factor at 1,000 cycles	Resistivity
	Time	Temperature			
Smoked sheet, 96 per cent; sulphur, 4 per cent.-----	Min.	° C		Per cent	Ohm-cm
	( <sup>1</sup> )	( <sup>1</sup> )	2.40	0.19	20×10 <sup>14</sup>
	40	155	2.74	.25	15
	60		2.82	.26	20
	90		2.87	.44	20
	120		2.88	.43	15
	185		2.94	.45	25
	305		2.70	.44	30
Smoked sheet, 92 per cent; sulphur, 8 per cent.-----	( <sup>1</sup> )	( <sup>1</sup> )	2.56	.25	25
	30	149	2.66	.38	180
	45		2.65	.37	40
	75		2.83	.37	25
	90		2.93	.29	25
	<sup>2</sup> 105		2.97	.32	30
	120		3.08	.38	30
	150		3.24	.79	50
	165		3.27	.90	50
	180		3.29	1.00	50
	20	155	2.67	.39	25
	30		2.74	.35	30
	45		2.78	.35	25
	60		2.92	.26	10
	<sup>3</sup> 75		3.03	.35	30
	95		3.30	.90	40
	140		3.46	1.47	45
	240		3.54	2.07	45
	15	160	2.71	.38	25
	20		2.77	.35	30
	30		2.81	.23	20
	40		2.96	.88	90
	<sup>3</sup> 45		3.02	.35	30
	60		3.18	.50	40

<sup>1</sup> Unvulcanized.<sup>2</sup> Optimum cure.

It can not be true over the whole range of rubber-sulphur compounds that increasing the per cent of combined sulphur produces a corresponding increase in the dielectric constant else hard rubber, which may contain 32 per cent of sulphur in combination, would have a very high dielectric constant, while as a matter of fact the dielectric constant of hard rubber is no larger than of some specimens containing only 8 per cent sulphur.

## X. ELECTRICAL PROPERTIES OF ACCELERATED RUBBER COMPOUNDS

Accelerators are used in the vulcanization of rubber because they give a product having better and more uniform physical properties with shorter time of vulcanization. In this investigation several accelerators have been employed without noting any decided difference in the electrical properties of the resulting specimens. The use of rapid accelerators greatly facilitated the preparation of specimens. In preparing the specimens for the investigation of the properties of fillers and softeners, tetra-methyl-thiuram disulphide was used almost exclusively as an accelerator. Hence the effect of it on rubber compounds has been carefully studied.

Tetra-methyl-thiuram disulphide,<sup>10</sup> which is referred to simply as thiuram in this paper, is a substance of the chemical composition,  $[(CH_3)_2NCS]_2S_2$ . Not only may this substance be used as an accelerator with sulphur, but also it is capable of effecting vulcanization in the absence of free sulphur. In the latter case one-fourth of the sulphur which the thiuram contains enters into combination with the rubber, so evidently one of the four atoms of sulphur<sup>11</sup> is set free in a form available for vulcanization.

Vulcanization with the aid of thiuram, and with most other accelerators as well, differs from vulcanization with sulphur alone, in that good physical properties are obtained with a relatively small proportion of combined sulphur. For example, when a mixture of 92 per cent rubber and 8 per cent sulphur is vulcanized to a state of good cure, it usually contains about 3 or 4 per cent of combined sulphur; but equally good, if not better, physical properties result when vulcanization is effected by 2 per cent sulphur and  $\frac{1}{4}$  per cent of thiuram, and in the latter case the combined sulphur is about  $1\frac{1}{4}$  per cent.

A very distinct advantage of an accelerator, such as thiuram, in an investigation like the present one is that by means of it an unusually flat cure may be obtained. This cure is flat as regards

<sup>10</sup> The preparation, properties, and use of this material are discussed by the following: E. Romani, *Giorn. chim. ind. appl.*, 3, p. 197; 1921; and C. A., 16, p. 854; 1922. A. A. Somerville, *India Rubber World*, 69, p. 15; 1923. Bedford and Winkelman, *Systematic Survey of Rubber Chemistry*, pp. 23-52; 1923.

<sup>11</sup> Bedford and Sebrell, *J. Ind. Eng. Chem.*, 14, p. 25; 1922.



electrical properties as well as mechanical properties. Accelerators of the group to which thiuram belongs require the presence of zinc oxide to activate them. This is a slight disadvantage from the standpoint of electrical measurements in that it introduces another variable into the composition, but it will be shown in a later section that the effect of small percentages of zinc oxide on the electrical properties is slight.

The results on compounds containing thiuram can be classified under two headings: (1) Those in which the vulcanization was carried out by the thiuram alone; (2) those in which mixtures thiuram and sulphur were used.

### 1. COMPOUNDS VULCANIZED BY THIURAM ALONE

The results of the measurements on rubber-thiuram compounds are given in Table 10. In no case does the time of vulcanization at a definite temperature have an appreciable effect on any of the electrical constants of any of the compounds. However, the results are affected by the percentage of thiuram and possibly by the temperature of vulcanization.

The dielectric constant of a rubber-thiuram compound increases as the percentage of thiuram increases. This is shown in Figure 14

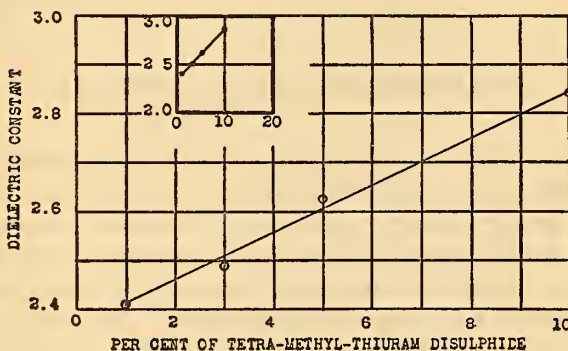


FIG. 14.—Effect of thiuram on the dielectric constant of rubber compounds

Insert shows the curve drawn to the same scale as used in Figure 15

where the per cent of thiuram is plotted against the dielectric constant. No correction has been made for the varying amounts of zinc oxide. The dielectric constant shows a linear increase with the per cent of thiuram. There is no appreciable change with changes either in time or temperature of vulcanization.

The power factor and resistivity apparently bear no relation to the per cent of the thiuram, nor do they vary with the time of cure, at a given temperature. There does seem, however, to be a difference in respect to these constants between specimens vulcanized at 155° C. and those vulcanized at 126° C., which is not dependent on the composition of the sample. More data are necessary before an explanation can be made.

TABLE 10.—*Electrical measurements on compounds vulcanized with thiuram in varying proportions*

Composition			Vulcanization		Dielectric constant at 1,000 cycles	Power factor	Resistivity
Rubber	Thiuram	ZnO	Time	Temperature			
<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Min.</i>	<i>° C.</i>		<i>Per cent</i>	<i>Ohm-cm</i>
98	1	1	45 90	155	{ 2.42	0.87 .81	185×10 <sup>14</sup> 195
					{ 2.40		
					(Av.) 2.41	.84	190
92	5	3	15 40	126	{ 2.49	.42 .40	20 24
					{ 2.48		
					(Av.) 2.49	.41	22
85	10	5	4 12	155	{ 2.60	.90 .80	200 220
					{ 2.59		
					(Av.) 2.60	.85	210
85	10	5	20 30 40	126	{ 2.66	.47 .48 .45	20 50 20
					{ 2.65		
					{ 2.62		
80	10	10	20	126	(Av.) 2.64	.47	30
					2.84	.50	5

2. COMPOUNDS VULCANIZED BY MIXTURES OF THIURAM AND SULPHUR

In order to investigate the effect of thiuram when used as an accelerator along with sulphur, a series of compounds was prepared starting with one vulcanized by means of thiuram alone, and going through compounds in which thiuram was used in decreasing amounts and sulphur in increasing amounts, to a compound which was vulcanized by means of sulphur alone. The relative amounts of sulphur and thiuram were so chosen that the mechanical properties of the resulting vulcanized rubber was approximately the same in all cases. The series extended from a compound vulcanized with 3 per cent thiuram to one cured with 4 per cent of sulphur. The results in this series are given in Table 11.

For small amounts of sulphur, the dielectric constant is the same for all the compounds, and does not differ much from that of crude rubber. This is to be expected since they all contain only very small proportions of combined sulphur. Moreover, for these compounds, the dielectric constant is independent of the time of cure. For amounts of sulphur equal to 4 per cent or more, the dielectric constant increased with increasing amounts of sulphur. Also, there was an increase in dielectric constant with increasing time of vulcanization. Apparently when the proportion of sulphur to accelerator is relatively large, as in case of the compound containing 4 per cent sulphur and ¼ per cent of thiuram, the vulcanization reaction is not complete in a very short time, but continues over a considerable range so that the cure is no longer "flat."

TABLE 11.—The electrical properties of rubber compounds vulcanized with different proportions of sulphur and thiuram

Composition				Vulcanization		Dielectric constant at 1,000 cycles	Power factor at 1,000 cycles	Resistivity
Rubber	Sulphur	Thiuram	ZnO	Time	Temperature			
<i>Per cent</i> 92	<i>Per cent</i> 0	<i>Per cent</i> 3	<i>Per cent</i> 5	<i>Min.</i> 15 40	<i>° C.</i> 126	2.49 2.48	<i>Per cent</i> 0.41 .40	<i>Ohm-cm</i> 19×10 <sup>14</sup> 24
						(Av.) 2.49	.41	22
91¾	¼	3	5	20 30 35	126	2.48 2.47 2.45	.40 .26 .26	27 44 45
						(Av.) 2.47	.31	40
92½	½	2	5	10 15 20 25 30 40	126	2.51 2.47 2.54 2.61 2.46 2.48	.23 .24 .23 .23 .37 .35	150 160 160 120 70 80
						(Av.) 2.51	.27	125
92¾	1½	¾	5	10 15 20 25	126	2.49 2.57 2.55 2.49	.35 .35 .34 .34	150 110 130 210
						(Av.) 2.52	.35	150
90¾	4	¾	5	15 20 25 30	126	2.60 2.67 2.73 2.78	.23 .26 .32 .41	90 80 20 10
						(Av.) 2.70	.30	50
96	4	?	?	60 90 120 185	155	2.82 2.87 2.88 2.94	.26 .44 .43 .45	19 19 16 25
						(Av.) 2.88	.40	20

The power factor and resistivity show no marked change with change in composition. With the compounds containing 4 per cent sulphur there is, however, an increase in power factor with increasing time of vulcanization.

## XI. EFFECT OF SOFTENERS ON THE ELECTRICAL PROPERTIES OF RUBBER

The electrical constants of compounds made with softeners are not greatly different from those made without them. Values of the constants for two different base compounds and for mixtures of these compounds with various softeners are given in Table 12. The values given are the average of those in two samples except in some of the resistivity values. Where the two values differed very widely, both values are given. The dielectric constant of rubber compounds is changed slightly, if at all, by the addition of ozokerite, vaseline, beeswax, palm oil, or stearic acid. There was a slight increase when



commercial paracoumarone resin was used, and also with large amounts of mineral rubber. However, the former contained some inorganic salts and even traces of sulphuric acid, while the latter contained amorphous carbon. The power factor was increased by the presence of all the softeners except ozokerite. Ozokerite did not affect the power factor. With the other materials the power factor was about doubled, except with paracoumarone resin, which trebled it.

The resistivity of specimens with softeners was very variable. This may have been caused by the "blooming" of the wax, producing a layer of very high resistivity on the surface.

TABLE 12.—*The effect of softeners on the electrical properties of rubber at optimum cure*

Base compound	Softener added	Vulcanization		Dielectric constant at 1,000 cycles	Power factor at 1,000 cycles	Resistivity
		Time	Temperature			
		<i>Min.</i>	<i>° C.</i>		<i>Per cent</i>	<i>Ohm-cm</i> <i>90×10<sup>14</sup></i>
Rubber, 90¼ per cent; ZnO, 5 per cent; sulphur, 4 per cent, and thiuram, ¼ per cent.	None.....	20	126	2.67	0.27	170
	3 per cent ozokerite.....	20	126	2.63	.25	20-215
	10 per cent vaseline.....	20	126	2.71	.50	2-6,400
	10 per cent beeswax.....	20	126	2.65	.61	3-30
	5 per cent palm oil.....	15	126	2.76	.40	40-90
	2 per cent stearic acid.....	20	126	2.78	.45	125
	10 per cent stearic acid.....	20	126	2.61	.41	
Rubber, 88 per cent; ZnO, 9 per cent; sulphur, ¼ per cent, and thiuram, 3 per cent.	None.....	10	132	2.58	.42	180
	10 per cent ozokerite.....	10	132	2.57	.42	14
	10 per cent paracoumarone resin.....	10	132	2.88	.81	3
	33 per cent mineral rubber.....	12	132	2.80	.59	5

## XII. ELECTRICAL PROPERTIES OF VULCANIZED RUBBER CONTAINING FILLERS

Investigation of the effect of fillers on the electrical properties of rubber is of particular interest on account of the extent to which fillers are used in the compounding of commercial rubber insulation for wire and cable. For many purposes, where strength and elasticity are of secondary importance, the amount of rubber in the insulation compound may be only 20 per cent, the remainder of the composition being largely made up of inert filling materials. Even in the highest grade of rubber insulation there is seldom more than 40 per cent rubber. Hence the characteristics of the filler generally are of much more consequence in determining the properties of a rubber insulation than are the characteristics of rubber itself. The other factors in the composition and preparation of rubber insulation, such as the kind of crude rubber, the accelerator or softener, or the conditions of vulcanization are generally of far less consequence than the kind and amount of filler.

In general, the electrical properties of a compound containing a filler are intermediate between those of the filler and those of the rubber. For instance, the common fillers are inorganic substances which have higher dielectric constants than rubber itself, so the use of fillers increases the dielectric constant of a rubber compound. Carbon has a relatively low resistivity as compared with rubber, so the use of carbon in a rubber compound decreases the resistivity.

No attempt has been made to investigate the properties of all the fillers in common use. The fillers which have been studied over a range of proportions are zinc oxide, litharge, carbon, quartz, and selenium. Zinc oxide is of particular interest because of the very general application which it finds in rubber compounding. Many accelerators, such as thiuram, will not function unless zinc oxide is present in small amounts as an activator. In larger amounts, as a filler, zinc oxide imparts strength and resistance to abrasive wear of rubber. Litharge has a twofold function in that it may serve both as an accelerator and as a filler. In this investigation it has been studied over a wide range of composition, in which its effect is chiefly that of a filler. Carbon is a filler which imparts good mechanical properties to rubber similar to those given by zinc oxide, but the electrical properties imparted by carbon are very different from those given by any other filler. It is the only filler in common use which is electrically conducting. Interest in quartz as a filler lies in the fact that it has many desirable electrical characteristics, and its electrical constants are known. Selenium was included because of its chemical similarity to sulphur, and also because it is one of few non-metallic elements which can be incorporated in rubber in a wide range of proportions. In addition to the above-mentioned substances, single compounds have been made with several other fillers, and their electrical constants determined.

### 1. ZINC OXIDE

The results of measurements on compounds containing zinc oxide as a filler are given in summarized form in Table 13. For the sake of simplicity and brevity, all the measurements on a given compound are averaged together. This is possible since there was little variation due to differences in time of cure of different specimens. The variations which were encountered between different specimens are indicated in the table by giving the range of values obtained for each compound as well as the average value. In case of the dielectric constant, part of the variation was due to differences in cure, but the average value is that for optimum cure. In case of the power factor and resistivity, the values, which showed sometimes rather large variations, are not affected by the time of cure.

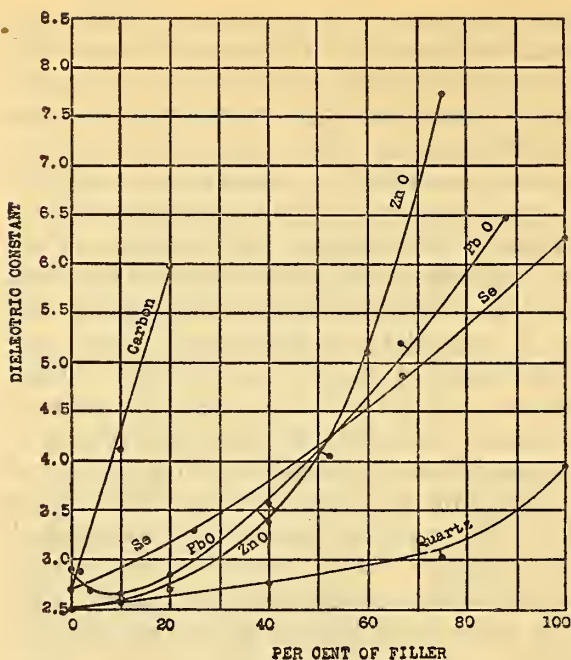


FIG. 15.—Effect of fillers on the dielectric constant of rubber compounds

The results show that the filler has a marked effect on the dielectric constant. This increases from 2.50 with 1 per cent of zinc oxide to 7.7 with 75 per cent of zinc oxide. The way in which the dielectric constant varies with the proportion of zinc oxide by weight is shown graphically in Figure 15. Up to 20 per cent of zinc oxide, the effect of the filler on the dielectric constant is slight, and it is clear that the small amount of zinc oxide needed to acti-

vate an accelerator would lead to only a slight increase in the dielectric constant.

The power factor shows a slight increase with increasing amounts of zinc oxide. The results are shown graphically in Figure 16. However, there is some uncertainty whether the observed increase is really due to zinc oxide or to traces of moisture which were not removed from it.

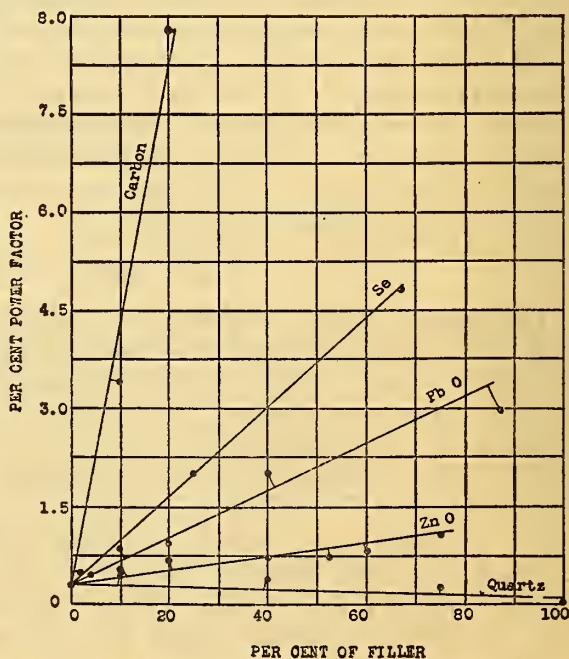


FIG. 16.—Effect of fillers on the power factor of rubber compounds



TABLE 13.—The electrical properties of compounds containing zinc oxide as a filler

Per cent of ZnO	Range of cure at 126°	Type of electrode	Number of specimens	Dielectric constant at 1,000 cycles			Power factor at 1,000 cycles			Resistivity		
				Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean
1-----	Minutes 15-40	Embedded metal.	8	2.43	2.56	2.50	Per cent 0.23	Per cent 0.38	Per cent 0.33	Ohm-cm $25 \times 10^{14}$	Ohm-cm $60 \times 10^{14}$	Ohm-cm $45 \times 10^{14}$
1-----	15-25	Water-----	9	2.49	2.57	2.50	.47	.73	.61	35	220	105
10-----	15-20	do-----	4	2.55	2.68	2.61	.47	.58	.52	65	135	95
20-----	15-20	do-----	8	2.67	2.73	2.70	.55	.76	.67	110	240	180
40-----	10-45	do-----	8	3.52	3.63	3.57	.52	.79	.71	85	180	150
52½-----	15-30	do-----	3	3.92	4.14	4.03	.46	.49	.48	55	70	60
60-----	15-20	do-----	4	4.92	5.12	5.01	.73	.87	.81	20	45	35
75-----	15-30	do-----	7	7.40	8.02	7.72	.99	1.16	1.05	3	12	7

Base compound used for the above specimens:

Per cent

Pale crêpe-----	93¾
Palm oil-----	4
Sulphur-----	2
Thiuram-----	¼

The variation in resistivity measurements up to 40 per cent of zinc oxide may be due to incidental causes, because similar variations were encountered between different specimens of the first compound. But the values found for the resistivity of compounds containing 60 and 75 per cent zinc oxide indicate that in these proportions the filler effects a slight reduction in the resistivity of the compound. This is to be expected, since zinc oxide, measured in the form of a loose powder, showed a resistivity of the order of  $10^{11}$  ohm-cm, which is very decidedly lower than that of rubber.

## 2. LITHARGE

A study of the effect of litharge on the electrical properties of rubber is complicated not only by the double rôle of the material as an accelerator and a filler, but also by the fact that a certain amount of litharge combines with sulphur to form lead sulphide and lead sulphate, and thus renders some of the sulphur not available for purposes of vulcanization. Since there seems to be no simple way to determine in advance how much sulphur will react with litharge, it is not easy to prepare a series of compounds high in litharge in which the proportion of available sulphur is constant. The compounds to which reference is made in Table 14 are not strictly comparable in that some have a larger proportion of available sulphur than others, but the effect of litharge is relatively so large as to overshadow the variations attendant on different states of vulcanization.

The relation of the dielectric constant to the per cent of litharge is shown graphically in Figure 15. The values of the dielectric constant used are those for specimens at optimum cure. Small amounts of litharge give a product having a lower dielectric constant

than the comparable rubber-sulphur compound, and only with 20 per cent of litharge does the dielectric constant equal in value that of the unaccelerated compound. In case of higher percentages of litharge, however, there is a rapid increase in the dielectric constant with increasing percentages of the material.

Even small amounts of litharge in a compound increase the power factor. There is also some indication that the power factor increases with increasing time of vulcanization. The values plotted in Figure 16 are for approximate optimum cure. The value for 66.7 per cent litharge was omitted from the plot, as it has a value too high to be shown advantageously.

The resistivity of compounds containing small amounts of litharge is greater than that of comparable rubber-sulphur compounds. Only with a compound having 88 per cent of litharge does the resistivity fall below the usual range for rubber compounds.

TABLE 14.—The electrical properties of compounds containing litharge (PbO)

Composition <sup>1</sup>				Vulcanization		Dielectric constant at 1,000 cycles	Power factor at 1,000 cycles	Resistivity
Rubber	Softener	PbO	S	Time	Temperature			
Per cent 96	Per cent 0	Per cent 0	Per cent 4	Min. 60 60 90 120 185	° C. 155	2.82 2.87 2.88 2.94	Per cent 0.26 0.44 0.43 0.45	Ohm-cm 20×10 <sup>14</sup> 20 15 25
88	4	4	4	30 45	142	2.69 2.68	.46 .45	250
				10		2.64	.81	135
				15	142	2.65	.84	195
82	4	10	4	20		2.66	.86	170
				10		2.74	.79	70
				12	142	2.77	.76	75
74	0	20	6	15		2.87	1.28	110
				20		3.00	1.43	85
				10	142	3.13	2.28	250
52	0	40	8	12		3.40	2.3	190
				15		3.58	1.8	250
				20	142	3.48	1.8	240
22	1	66	11	7		5.21	7.4	40
				15		6.96	3.2	45
				10	142	6.48	3.0	0.02

<sup>1</sup> Materials used: Rubber, smoked sheet; softener, ozokerite for first two compounds and palm oil for the last two.  
<sup>2</sup> Approximate optimum cure.

3. CARBON

Carbon has a greater effect on the electrical properties of rubber than any of the other fillers which have been investigated. In fact, with the introduction of a large percentage of carbon into rubber, the conductivity increases to such an extent that the dielectric constant and power factor have little meaning, and only the resistivity can be measured.

Carbon black is the form in which carbon is commonly used in rubber compounding. This consists of carbon particles in an extremely fine state of subdivision. The effect on the electrical con-

stants of incorporating varying percentages of carbon black in rubber is shown in Table 15. As little as 0.2 per cent of carbon has a perceptible effect on the dielectric constant. With 20 per cent the dielectric constant is more than double that of the base compound. This effect is shown graphically in Figure 15. The increase in dielectric constant is almost linear, and it is much greater than with equal amounts of other fillers.

The effect of carbon on the power factor is of even greater relative magnitude than the effect on the dielectric constant. With 10 per cent of carbon, the power factor is about 10 times that of the base compound, and with 20 per cent carbon it is nearly 30 times that of the base compound. This very pronounced effect is shown in comparison with other fillers in Figure 16.

The introduction of carbon greatly decreases the resistivity of rubber. This effect is not apparent, however, with 0.2 to 2 per cent of carbon. With 10 per cent of carbon some of the specimens show a resistivity of  $20 \times 10^{14}$  ohm-cm, which is not lower than that of some pure rubber compounds. At higher percentages of carbon, however, the resistivity falls off with greater rapidity.

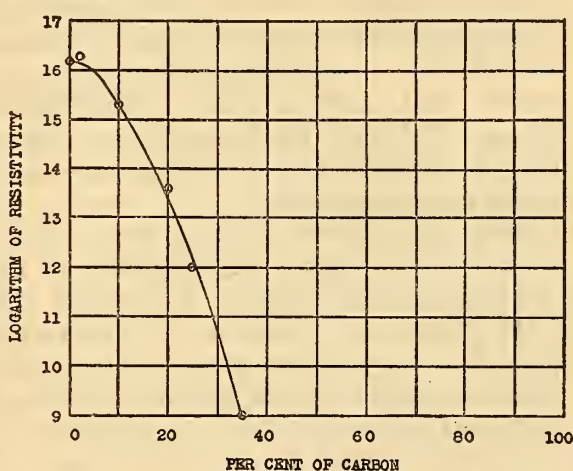


FIG. 17.—Effect of carbon on the resistivity of rubber compounds

In plotting the curve in Figure 17 showing the change in resistivity with percentage of carbon, the highest observed values have been used for the resistivity rather than average values. These were selected since there are factors both in the preparation of the specimen and in the electrical measurements which tend to make the observed value of the resistivity lower than the true one, and no factors which might have the reverse effect.



TABLE 15.—*The electrical properties of compounds containing carbon*

Percentage of carbon black	Number of specimens	Dielectric constant at 1,000 cycles			Power factor at 1,000 cycles			Resistivity	
		Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum
0.....	6	2.58	2.74	2.68	<i>Per cent</i> 0.23	<i>Per cent</i> 0.41	<i>Per cent</i> 0.29	<i>Ohm-cm</i> 80×10 <sup>14</sup>	<i>Ohm-cm</i> 150×10 <sup>14</sup>
0.2.....	5	2.66	2.82	2.73	.35	.56	.44	70	170
2.....	6	2.81	2.94	2.89	.40	.58	.48	100	190
10.....	4	4.01	4.23	4.11	3.0	3.9	3.4	7×10 <sup>13</sup>	190×10 <sup>13</sup>
20.....	3	5.73	6.22	5.97	6.9	9.8	8.8	2	4
25.....	5							1×10 <sup>12</sup>	11×10 <sup>12</sup>
35.....	6							3×10 <sup>6</sup>	30×10 <sup>6</sup>

## 4. QUARTZ

The electrical properties of rubber containing finely divided quartz as a filler are of interest, since quartz has a high resistivity and low dielectric loss. Accordingly a series of compounds were made with crushed fused quartz as a filler. This filler was prepared by grinding coarsely broken fused quartz in a ball mill with flint pebbles. It was not reduced to extreme fineness since the aim was to employ it simply as an inert filler.

Compounds containing the ground, fused quartz, even in large proportion, show only a slight departure in their electrical constants from pure gum compounds. A summary of the electrical measurements is given in Table 16. The constants of fused quartz are included in the table for purposes of comparison. In Figure 15 is shown the variation of the dielectric constant with composition over the range from pure rubber to pure quartz. Up to the composition, 75 per cent quartz–25 per cent rubber, the dielectric constant increases slowly and uniformly with increasing proportion of filler. Beyond this point, there must be a relatively sharp increase to reach the value of 100 per cent quartz.

The power factor of compounds containing quartz differs little from that of the base rubber compound. In this respect, quartz differs from most fillers, which are associated with an increase in the power factor.

The resistivity shows a slight decrease with increasing proportions. This is opposite to what would be expected, since quartz has a much higher resistivity than rubber. The observed results may be due to small amounts of impurities.

TABLE 16.—The electrical properties of rubber compound containing quartz as a filler

Percentage of quartz	Number of specimens	Dielectric constant at 1,000 cycles	Power factor at 1,000 cycles	Resistivity
			<i>Per cent</i>	<i>Ohm-cm</i>
0.....	8	2.50	0.33	105×10 <sup>14</sup>
10.....	8	2.57	.43	95
40.....	5	2.76	.38	40
75.....	2	3.03	.23	30
100.....		3.88	.01	About 10 <sup>10</sup>

Base compound:	Per cent
Pale crepe.....	92½
Zinc oxide.....	1
Palm oil.....	4
Sulphur.....	2
Thiuram.....	¼

Specimens were vulcanized for 12 to 25 minutes at 126° C. Variation in time of vulcanization produced only slight differences in electrical properties.

5. SELENIUM AND TELLURIUM

The electrical properties of rubber containing selenium and tellurium are given in Table 17. Values are also given for selenium. The dielectric constant of rubber compounds containing selenium increases with the selenium content, as shown by the curve in Figure 15. The power factor of these compounds increases very markedly with increasing amounts of selenium. However, the one sample of selenium which was tested showed a lower power factor than the rubber compound containing 67 per cent selenium. This result needs to be confirmed before any conclusions are based on it. Selenium has a lower resistivity than rubber and the rubber compounds containing selenium have values intermediate between those of the two components.

The compound containing 25 per cent of tellurium has a lower dielectric constant than that of the corresponding selenium compound, notwithstanding the fact that tellurium has the greater density which is generally associated with a higher dielectric constant. From the semimetallic character of tellurium, a high power factor and low resistivity of rubber compounds containing tellurium would be expected. However, the values of these constants do not differ markedly from those of the basic rubber compound.

TABLE 17.—*The electrical properties of compounds containing selenium and tellurium*

Percentage of selenium and tellurium	Number of specimens	Dielectric constant at 1,000 cycles	Power factor at 1,000 cycles	Resistivity
Selenium:			<i>Per cent</i>	<i>Ohm-cm</i>
0.....	6	2.70	0.30	$90 \times 10^{14}$
25.....	5	3.30	2.0	90
67.....	3	4.87	4.8	4
100.....	1	6.25	2.7	.6
Tellurium:				
25.....	4	3.20	.50	85

Base compound:	Per cent
Rubber.....	90¾
ZnO.....	5
Sulphur.....	4
Thiuram.....	¼

Specimens were vulcanized for 5 to 40 minutes at 126° C. Variation in time of vulcanization produced only slight differences in the electrical properties.

## 6. OTHER FILLERS

The results on barytes, titanox, iron oxide, and china clay are summarized in Table 18. The dielectric constant of compounds containing 50 per cent of the above materials is greater than compounds containing a like amount of quartz, but less than compounds containing like amounts of any of the other fillers which have been investigated. The material which gave the lowest dielectric constant was china clay; then came barytes and iron oxide, with titanox giving the highest value. Neither the power factor nor resistivity values are markedly different from the values obtained for other fillers.

TABLE 18.—*The electrical properties of rubber compounds containing various fillers*

Base compound	Filler	Number of specimens	Dielectric constant at 1,000 cycles	Power factor at 1,000 cycles	Resistivity
				<i>Per cent</i>	<i>Ohm-cm</i>
1.....	None.....	4	2.70	0.32	$90 \times 10^{14}$
1.....	45 per cent barytes.....	4	3.37	1.1	20
1.....	50 per cent titanox <sup>1</sup> .....	4	3.77	1.1	13
1.....	46 per cent iron oxide.....	4	3.61	1.39	30
2.....	None.....	1	2.62	.75	190
2.....	49 per cent china clay.....	3	3.27	1.13	170

<sup>1</sup> "Titanox" is a commercial pigment of the approximate composition: Titanium dioxide, 25 per cent; barium sulphate, 75 per cent.

Composition of base compounds:

No. 1	Per cent	No. 2	Per cent
Smoked sheet.....	90¾	Smoked sheet.....	90
Zinc oxide.....	5	Zinc oxide.....	5
Sulphur.....	4	Sulphur.....	4
Thiuram.....	¼	Diphenylguanidine.....	



## XIII. ABSORPTION OF WATER BY RUBBER

Although the fact that rubber absorbs water has been known for a long time, no attempt has been made to correlate and interpret the data until quite recently. The results of several investigations <sup>12</sup> relating to the absorption of water by rubber have been published while this investigation has been in progress.

When rubber, either crude or vulcanized, is immersed in distilled water it increases in weight on account of the absorption of water. The same effect is produced by exposure to water vapor near the saturation point. In order to obtain data concerning water absorption, specimens of vulcanized rubber were immersed in distilled water. These specimens were made from commercial grades of crude rubber, without any special preparation. They were all in the form of molded sheets from 0.3 to 0.6 mm in thickness. The majority of these took up from 10 to 20 per cent of water in six months at room temperature, while in some cases the absorption was as high as 40 per cent or as low as 5 per cent. But in no case, was there evidence that the absorption had reached an equilibrium.

The behavior of vulcanized rubber in a salt solution is very different from that in distilled water, in that the water absorption is much less and apparently reaches an equilibrium. When specimens similar to those considered above were immersed in 3 per cent sodium chloride solution, which is roughly comparable to sea water, they took up from 1 to 3 per cent of water in the space of a month at room temperature, and thereafter did not increase in weight.

Contrary to what might be expected, compounds containing waxes, such as ozokerite, palm oil, beeswax, and vaseline, or asphaltic materials, such as mineral rubber, show water absorption of about the same rate and extent as the base compounds from which they are prepared. Fillers decrease the apparent water absorption of a compound because the proportion of rubber is decreased. The conditions of vulcanization have an effect on water absorption. Well-cured specimens take up somewhat less water than do undercured or greatly overcured specimens under the same conditions.

The addition of water-soluble materials to a rubber compound increases the extent of water absorption. The presence of small amounts of soluble materials greatly increases the absorption of water. Compounds made from crude rubber which contains a considerable proportion of the soluble constituents of the latex have a much higher absorptive capacity than do compounds made from well-washed crude rubber. In agreement with this, compounds

<sup>12</sup> Andrews and Johnson, The absorption of water by rubber, *J. Am. Chem. Soc.*, 46, p. 640; 1924. Anon., Making rubber available for submarine cable insulation, *India Rubber J.* 68, p. 1157; 1924. Kirchhof, Combinations of water with rubber, *Kolloid Z.*, 35, p. 367; 1924; and *C. A.* 19, p. 1065; 1925. Blake, Absorption of water by rubber, presented before the division of rubber chemistry at the sixty-ninth meeting of the American Chemical Society, Baltimore, Md., Apr. 10, 1925.

made from latex-sprayed rubber show relatively the highest water absorption and those from pale crêpe the lowest.

In order to obtain rubber as free as possible from water-soluble materials, samples of pale crêpe and smoked sheet were very thoroughly washed on the washing mill. Vulcanized specimens pre-

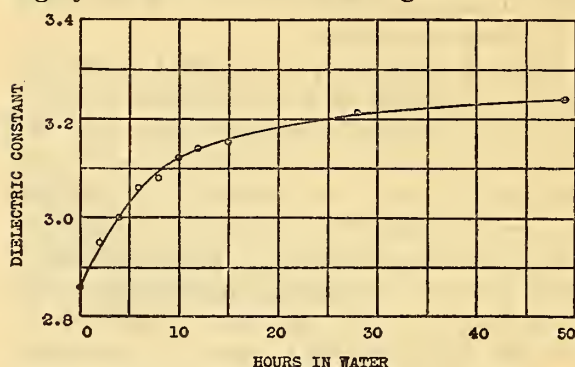


FIG. 18.—Effect of water absorption on the dielectric constant of a rubber compound

pared from this washed rubber increased in weight only 1 or 2 per cent when immersed in distilled water, and did not gain in weight at all in 3 per cent sodium chloride solution. This indicates that thorough washing of the crude rubber affords an effective practical means

of diminishing the absorption of water by a rubber product.

The use of water electrodes afforded a convenient means of following the changes in the electrical constants with time of immersion in water. Measurements were made on several specimens over a period of about two days during which time the electrical constants changed markedly. The results which are plotted in Figures 18, 19, and 20 were obtained when a specimen about 0.05 cm thick was tested with

tap water for the electrodes. The curves are characteristic of what was obtained on other specimens, though the values depended on the water absorptive properties of the different specimens. As shown in Figure

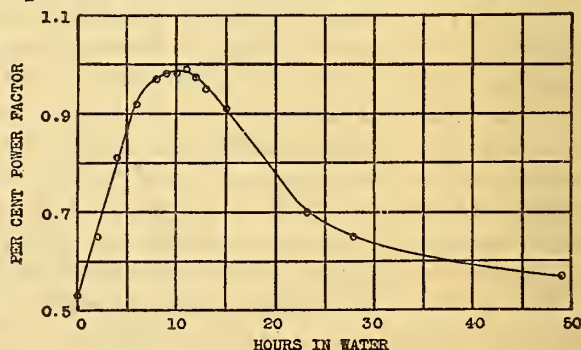


FIG. 19.—Effect of water absorption on the power factor of a rubber compound

18, the dielectric constant increased rapidly at first, then more slowly. The increase during the second day was only one-tenth of that during the first day. The power factor, as shown in Figure 19, nearly doubled in value in the first 10 hours, then began to decrease somewhat more slowly. At the end of two days the power factor was about the same as it was for the dried specimens. One specimen was observed for two weeks. After the

first 48 hours there was no material change. The resistivity decreased markedly during the first five hours, then slowly thereafter, as indicated by the curve in Figure 20.

In order to determine the effect of prolonged immersion in water, samples of vulcanized rubber and gutta-percha have been kept in tap water for nearly three years. These samples were made from commercial materials, many of them in commercial plants. The dielectric constant of all of them has increased with time, the increase being at an approximately uniform rate.

In three years gutta-percha and the best samples of rubber have increased about 10 per cent. Some of the poorer samples of rubber have increased over 30 per cent. Changes in the power factor and resistivity have not been marked. The interpretation of the data is difficult, since measurements were made at room temperatures, which varied considerably, and the temperature coefficient of both of these properties is large. The power factor of some specimens apparently increases and of others decreases. This applies to the gutta-percha samples as well as to the vulcanized rubber. Also, the resistivity apparently increases in some cases and decreases in others.

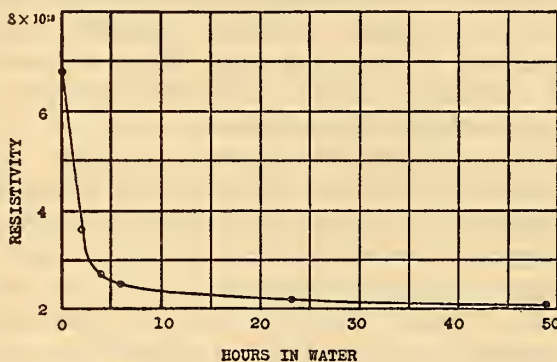


Fig. 20.—Effect of water absorption on the resistivity of a rubber compound

#### XIV. CONCLUSIONS

In order to obtain consistent and reliable measurements of the electrical constants of rubber and gutta-percha, attention must be paid to the form in which the specimens are prepared. Since water is a significant factor in the composition, it is necessary to dry specimens before measurements are made, unless the effect of water is specifically sought. Values of the dielectric constant and power factor depend upon the frequency. All values mentioned in these conclusions are based on measurements at 1,000 cycles.

##### 1. DIELECTRIC CONSTANT

The dielectric constant of crude rubber is lower than that of gutta-percha. The kind of crude rubber has only a small effect on the value, but wider variations are encountered between different kinds



of gutta-percha. With either material the more nearly the composition approaches that of the pure hydrocarbon the lower the dielectric constant. The lowest value found for rubber was 2.35 and for gutta, the hydrocarbon of gutta-percha, 2.58. For well-dried samples of commercial crude rubber values as high as 2.60 were obtained. For gutta-percha having a gutta content of 57 per cent the value was 3.0. Sheet balata having a gutta content of 45 per cent was found to have a dielectric constant of 3.5.

Vulcanization increases the dielectric constant of rubber. To some extent the conditions of vulcanization and the percentage of sulphur employed determine the dielectric constant of vulcanized rubber. Compounds containing accelerators have lower dielectric constants than do similar compounds vulcanized with sulphur alone. Accelerated compounds in which a small amount of sulphur is used may possess good mechanical properties and yet have a dielectric constant which is not very different from that of crude rubber. A cure which is flat as regards mechanical properties is also flat for the electrical properties.

For ordinary soft-rubber compounds made from sulphur and rubber, those factors which increase the amount of sulphur in combination with rubber also increase the dielectric constant. With a compound containing 8 per cent of sulphur, the dielectric constant increases from 2.5 for the material in unvulcanized state to 3.5 for long overcure samples. For the same compound the dielectric constant at optimum cure was about 3.0 regardless of the particular time and temperature used to effect the cure. Vulcanization with 4 per cent of sulphur increased the dielectric constant much less than vulcanization with 8 per cent, the highest value obtained being about 2.9. However, it can not be true that the dielectric constant of vulcanized rubber is a simple function of the percentage of combined sulphur because hard rubber has a dielectric constant lower than that of some compounds containing only 8 per cent of sulphur.

Softeners do not have much effect on the dielectric constant of a rubber compound, but fillers usually have a very pronounced effect. In general, fillers increase the dielectric constant, the extent depending on the amount used and the characteristics of the filler.

With approximately 50 per cent filler, the following values of the dielectric constant have been obtained:

Quartz.....	2.7	Titanox.....	3.8
China clay.....	3.3	Zinc oxide.....	4.0
Barytes.....	3.4	Litharge.....	4.1
Iron oxide.....	3.6	Selenium.....	4.2

However, the effect is not in all cases linear. This is shown by comparing the following values obtained with 70 per cent filler with those given above:

Zinc oxide.....	7.5
Litharge.....	5.5
Selenium.....	5.0

Carbon, which is a conducting material, produces very large changes in the dielectric constant; with 20 per cent carbon, the value is 6.0.

## 2. POWER FACTOR

The limiting lower values for the power factor of crude rubber and gutta are about the same, being 0.1 per cent. In case of either material, the power factor is increased by the presence of moisture. The power factor of gutta-percha also depends on the proportion of gutta to resin, being increased by the latter component. Samples of commercial material generally have a value of 1.5 per cent.

Vulcanization increases the power factor of rubber, the increase depending on the amount of sulphur and the extent of vulcanization. In the case of well-cured specimens made with 2 per cent of sulphur aided by an accelerator, the power factor is about 0.3 per cent; those made with both 4 and 8 per cent of sulphur and no accelerator have a value of about 0.4 per cent. However, on overcure, specimens with 8 per cent sulphur may have values of 1 or 2 per cent.

Most fillers increase the power factor. With carbon, the increase is very large. For 20 per cent carbon, the value is 8 per cent or more than twenty-five times the value of the base compound.

Values for compounds with 50 per cent filler are:

	Per cent
Selenium.....	3.7
Litharge.....	2.0
Zinc oxide.....	.7
Quartz.....	.2

The value for quartz is exceptional in that it is less than the base compound.

With small amounts of absorbed water, the power factor of vulcanized rubber may be double that of the dried sample. However, the addition of still more water decreases the power factor. When saturation is reached, the value is not materially different from the dried sample.

## 3. RESISTIVITY

The resistivity of both crude rubber and gutta-percha are subject to considerable variation, depending on the source and composition of these materials. The range of resistivity values is the same for the two materials, which is from  $10^{14}$  to  $10^{16}$  ohm-cm. Vulcanization

does not greatly change the resistivity of rubber, nor do most compounding ingredients when added in moderate amounts. The use of litharge in some proportions, however, increases the resistivity by a factor of 10. On the other hand, carbon as a filler brings about a considerable decrease, a value as low as  $10^8$  being obtained for a 35 per cent carbon.

#### 4. SUBMARINE CABLE INSULATION

From the standpoint of the electrical constants of the materials, rubber insulation may be made which is superior to gutta-percha as an insulation for submarine cables.

The authors wish to acknowledge assistance from a large number of their coworkers at the Bureau of Standards. Most of the electrical measurements have been made by Miss Johanna Busse and A. H. Scott.

WASHINGTON, May 23, 1925.

























